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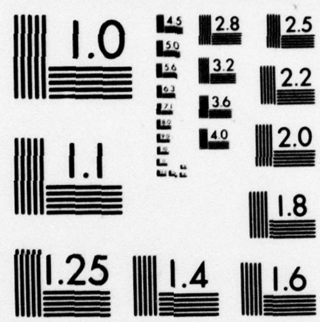

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UV/OZONE OXIDATION TECHNOLOGY DEVELOPMENT FOR WATER TREATMENT FOR FIELD ARMY MEDICAL FACILITIES

TECHNICAL REPORT

by

M.K. Lee and P.Y. Yang

July, 1978

Project Officers:
Major Walter P. Lambert and William J. Cooper
Environmental Protection Research Division
US Army Medical Bioengineering
Research and Development Laboratory
Ft. Detrick, Frederick, MD 21701

Supported by

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Ft. Detrick, Frederick, MD 21701

Contract DAMD17-76-C-6063

Life Systems, Inc.
Cleveland, OH 44122

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Prepared Under Contract No. DAMD17-76-C-6063

by

LIFE SYSTEMS, INC.
Cleveland, OH 44122

for

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Ft. Detrick, Frederick, MD 21701

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A pilot plant of an integrated water processing system has been developed. The Water Processing System treats nonsanitary wastewaters of the U. S. Army field hospitals either for nonpotable reuse or for surface discharge to the environment and purifies natural fresh and brackish waters for potable use. The Water Processing System consists of four units: (1) a Water Treatment Unit, (2) a Water Purification Unit, (3) a UV/Ozone Oxidation (O_3/UV) Unit and (4)

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an Automatic Instrumentation Unit. This report describes the development of the O_3/UV Unit. Emphasis has been placed on the UV/ozone oxidation technology developed for the design of the O_3/UV Unit.

The main objective of the O_3/UV Unit is to destroy and eliminate organic contaminants in water. It was designed for the contaminant removal efficiencies of not less than 84% for total organic carbon and 91% for chemical oxygen demand. The maximum achievable efficiencies anticipated for the hospital composite waste are approximately 97% for total organic carbon and 98% for chemical oxygen demand. The unit was sized to treat the hospital wastewaters at a rate of 3,500 gal/day for reuse and 3,900 gal/day for surface discharge. It operates 20 hours a day at a product water recovery of 99.5%. The overall dimensions of the transportable O_3/UV Unit are 10 x 8.5 x 6.75 ft.

The UV/ozone oxidation is a chemical treatment process in which organic impurities, including carcinogens and other pathogens are oxidized to harmless carbon dioxide and water by ozone and ultraviolet light. It also can provide a 100% killing of bacteria, viruses and other microorganisms, a complete destruction of color and odor, and an improvement of taste. Results of the UV/ozone oxidation kinetic study indicated that the reduction rate of total organic carbon is first-order with respect to the total organic carbon concentration. It was also found that the reaction rate has 1.5th-order dependence on the ozone partial pressure and the air superficial velocity. Based on the results a reactor design equation was developed to scale-up the ozone contactor for the full-scale pilot plant.

EXECUTIVE SUMMARY

American soldiers do not question the quality of the water that comes out of the tap. They drink and shower daily without any suspicion. Limited sources of natural fresh water, together with the possibility of ground water poisoning by the enemy, make the reclamation of wastewater for reuse extremely vital to the operation of the combat unit and the Army field hospital in water-deficient areas. In response to this need, the U.S. Army Medical Research and Development Command has been developing a wastewater reuse system known as a water processing element. The interim objective is reuse of nonsanitary wastewaters for nonpotable hospital requirements. The ultimate objective is reuse for potable and nonpotable requirements. Under this program a full-scale pilot plant of a water processing system was designed, built and delivered to the Army under Contract No. DAMD17-76-C-6063.

The Water Processing System has a nominal product water capacity of 3,500 gal/20-hour day. It consists of four units: (1) a Water Treatment Unit, (2) a Water Purification Unit, (3) an Ultraviolet/Ozone Oxidation Unit and (4) an Automatic Instrumentation Unit. The primary objective of this report is to describe the ultraviolet/ozone oxidation technology developed for treatment of the hospital wastewaters.

There are two types of composite wastes in the nonsanitary wastewaters produced in the field Army medical facilities. One is a hospital composite waste consisting of shower (51%), operating room (26%), kitchen (12%), laboratory (8%) and X-ray waste (3%). The other type is a laundry composite waste consisting of 67% Type I (color-fast) and 33% Type II (woolens). In addition to the above wastes, the Water Processing System treats natural fresh or brackish water for potable use. The projected variations of the contaminant concentrations in the hospital wastewaters are 50-1,000 mg/l for total organic carbon and suspended solids, 300-6,000 mg/l for chemical oxygen demand, 500-4,200 mg/l for total solids and 5-900 JTU for turbidity.

The Water Processing System consists of two modes of operation: Reuse Mode and Potable/Discharge Mode. In the Reuse Mode the Water Processing System treats and purifies the nonsanitary hospital wastewaters for nonpotable reuse. In the Potable/Discharge Mode it simultaneously treats those wastewaters for safe discharge to the environment while treating natural waters for potable use. The overall product recovery is at least 85% of inflow in the Reuse Mode and 90-95% in the Potable/Discharge Mode. The overall contaminant removal efficiencies are 98.9% for total organic carbon, 99.5% for chemical oxygen demand and 98.5% for total solids.

The Water Processing System pilot plant is one of the most advanced water treatment systems in which a number of state-of-the-art technologies and the most recent advances in water processing have been integrated into a compact design. It has many of the prototype Water Processing System features which can be transported to a point of mission via conventional routes such as standard cargo trucks, external helicopter loads, railroad, ship or cargo aircraft. In addition to treatment of the field Army hospital wastewaters and the natural waters, the pilot plant also can be used as a test bed for the general purpose of water treatment.

The main objective of the Ultraviolet/Ozone Oxidation Unit is to destroy and eliminate organic contaminants in water. In the Reuse Mode the Ultraviolet/Ozone Oxidation Unit is the third treatment unit for the hospital wastewaters pretreated in both the Water Treatment Unit and the Water Purification Unit. In the Potable/Discharge Mode it serves as a supplementary unit of the Water Treatment Unit to produce a safe discharge water from certain hospital wastewaters with high organic concentrations. The Ultraviolet/Ozone Oxidation Unit was designed for its contaminant removal efficiencies not to be less than 84% for total organic carbon and 91% for chemical oxygen demand. The maximum achievable efficiencies anticipated for the hospital composite waste are approximately 97% for total organic carbon and 98% for chemical oxygen demand.

The ultraviolet/ozone oxidation is a chemical treatment process in which organic impurities, including carcinogens and other pathogens, are oxidized to harmless carbon dioxide and water by ozone and ultraviolet light. It also can provide a 100% killing of bacteria, viruses and other microorganisms, a complete destruction of color and odor, and an improvement of taste. Results of the ultraviolet/ozone oxidation kinetic study indicated that the reduction rate of total organic carbon is first-order with respect to the total organic carbon concentration. It was also found that the reaction rate has 1.5th-order dependence on the ozone partial pressure and the air superficial velocity. Based on the results a reactor design equation was developed to scale-up the ozone contactor for the full-scale pilot plant.

The Ultraviolet/Ozone Oxidation Unit was sized to treat the hospital wastewaters at a rate of 3,500 gal/day for reuse and 3,900 gal/day for surface discharge. It operated 20 hours a day at a product water recovery of 99.5%. The unique requirements for the design were: (1) limited allowance on dimensions, weight and power consumption for transportation and field application; (2) automatic instrumentation and mimimum maintenance for unskilled operators; and (3) pilot plant capabilities and semiautomatic instrumentation for performance evaluation and scientific data development.

The major components of the Ultraviolet/Ozone Oxidation Unit are an ozone generator, a precontactor and a six-stage ozone contactor. The ozone generator produces 25 lb ozone (at 1% by weight) from air. An air compressor feeds 24 scfm of air at 60 psig through drying columns to the ozone generator. The precontactor has a wet volume of 100 gal to provide a 33-minute space time (mean residence time) for water. The ozone contactor is composed of three reactor modules. Each module, consisting of two stages, is 60 x 10 x 78 inches and contains 20 ultraviolet lamps. Each contactor stage has its own sparger which is fabricated from a porous sintered stainless steel plate with a 5 micron pore size. The total wet volume of the ozone contactor is 544 gal. The overall dimensions of the transportable, Ultraviolet/Ozone Oxidation Unit are 10 x 8.5 x 6.75 ft. The unit is configured so all components are easily accessible.

Both automatic and semiautomatic instrumentations were incorporated into the Ultraviolet/Ozone Oxidation Unit design to control and monitor the system performance. Only the semiautomatic instrumentation is described in this report. The semiautomatic instrumentation is highlighted by seven automatic fail-safe shutdown controls, eight digital readout monitors, ten warning and alarm lights and 26 controls for pumps, valves and ultraviolet lamps.

FOREWORD

This study was conducted, as part of the Water Processing System pilot plant development, for the U. S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD, under Contract No. DAMD17-76-C-6063. The Program Manager was Dr. R. A. Wynveen. Technical effort was completed by Dr. M. K. Lee, Dr. P. Y. Yang, D. C. Walter, G. G. See and T. S. Steenson.

Maj. W. P. Lambert and Mr. W. J. Cooper, Environmental Protection Research Division, U. S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD, were the Technical Monitors of this program. We also wish to acknowledge the technical contributions, assistance and program guidance offered by Lt. Col. L. H. Reuter, Maj. W. P. Lambert and Capt. J. J. McCarthy.

Results of the pilot plant development program have been published in six reports as follows:

Title	Report No.
Pilot Plan Development of an Automated, Transportable Water Processing System for Field Army Medical Facilities	ER-314-7-1
Water Treatment Unit Development for Field Army Medical Facilities	ER-314-7-2
Water Purification Unit Development for Field Army Medical Facilities	ER-314-7-3
Advanced Instrumentation Development for a Water Processing Pilot Plant for Field Army Medical Facilities	ER-314-7-4
UV/Ozone Oxidation Technology Development for Water Treatment for Field Army Medical Facilities	ER-314-7-5
Data Acquisition, Monitor and Control System Development for Field Army Medical Facilities	ER-314-7-6

The first report, ER-314-7-1, outlines the overall program for the pilot plant development of the Water Processing System. The succeeding reports present further details on the subsystem developments of the Water Processing System pilot plant. The pilot plant consists of four subsystems: (1) a Water Treatment Unit, (2) a Water Purification Unit, (3) a UV/Ozone Oxidation Unit and (4) an Automatic Instrumentation Unit. This report covers the development of the UV/Ozone Oxidation Unit and its associated technology.

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ACRONYMS

COD	Chemical Oxygen Demand
EP	Equalization and Prescreening
HC	Hypochlorination
JTU	Jackson Turbidity Unit
O_3/UV	UV/Ozone Oxidation
RO	Reverse Osmosis
TOC	Total Organic Carbon
UF	Ultrafiltration
USAMRDC	U.S. Army Medical Research and Development Command
WPS	Water Processing System
WPU	Water Purification Unit
WTU	Water Treatment Unit

INTRODUCTION

A sufficient, reliable supply of safe drinking water has played one of the most important roles in fighting in water-deficient areas such as Africa and Indochina during World War II, and in Vietnam and the Middle East Asia. Recently, a safe water supply has been recognized as important to the success of the U. S. Army operation along with other expendable supplies such as ammunition and food. Unlike ammunition and food, safe drinking water can be produced on site near the battlefield and wastewaters generated in the Army installations can be recycled for reuse after treatment. Such water management may significantly reduce or ultimately eliminate the logistical burden of the Army operation associated with hauling a huge amount of water to each new field installation. In addition, it is not permissible that American soldiers' health and lives be in danger as a result of drinking natural waters poisoned by the enemy.

To ensure that tactical flexibility of the combat unit and the mobile field hospital should not be limited by fixed fresh water sources, the U. S. Army Medical Research and Development Command (USAMRDC) has been developing an advanced water processing system for the field Army medical facilities. The interim objective is reuse of nonsanitary hospital wastewaters for nonpotable hospital requirements.[1] The ultimate objective is reuse for potable and nonpotable requirements.

A full-scale pilot plant of an advanced Water Processing System (WPS) was designed and built by Life Systems, Inc. under Ccontract DAMD17-76-C-6063. The specific objectives of this program were to:

1. Design, fabricate, check out, deliver and start up a fully-functional WPS pilot plant.
2. Design, fabricate, test, install, start up and debug a Data Acquisition, Monitor and Control System.
3. Provide technical support to ensure the operability of the WPS pilot plant.

The WPS pilot plant consists of four subsystems: (1) a Water Treatment Unit (WTU), (2) Water Purification Unit (WPU), (3) an UV/Ozone Oxidation (O_3/UV) Unit and (4) an Automatic Instrumentation Unit.

The main purpose of this report is to describe the UV/ozone oxidation technology developed for the design of the O_3/UV Unit. This report is intended to be supplementary to Report, ER-314-7-1, which outlines the overall program for the pilot plant development.

WATER PROCESSING SYSTEM

The WPS is a fully automated, integrated water treatment system which fulfills three functional requirements: (1) potable water production from natural

(1) References cited at the end of this report.

waters; (2) nonpotable reuse water production from hospital wastewaters generated in the field Army medical facilities; and (3) treatment of the hospital wastewaters for safe discharge to the environment.

Figure 1 is a flow diagram of the WPS. Hospital wastewaters collected in the equalization tank are pumped through ultrafiltration (UF) membranes. Depending on the mode of operation, the permeate stream of the UF membranes is further purified for reuse by reverse osmosis (RO) membranes or discharged to the environment either through a hypochlorination (HC) unit (calcium hypochlorite mixers) or through an O_3 contactor and the HC unit. The permeate stream of the RO membranes flows to the reuse water storage tank either through the other HC unit (lower one) or through the O_3 contactor and the HC unit, depending on the organic content in the wastewater. Potable water is produced by purifying natural waters such as brackish surface water and fresh well water. The natural water purification follows a sequence of depth filtration, carbon adsorption, ion exchange, reverse osmosis and hypochlorination processes.

The WPS can be operated in either the Reuse Mode or the Potable/Discharge Mode (Table 1). In the Reuse Mode the WPS treats and purifies the nonsanitary hospital wastewaters for nonpotable reuse. In the Potable/Discharge Mode it simultaneously treats those same wastewaters for discharge to the environment while treating natural fresh or brackish water for potable use. The overall recovery of the product water is at least 85% of inflow in the Reuse Mode and 90-95% in the Potable/Discharge Mode.

Figure 2 is a block diagram of the Reuse Mode. Nonsanitary hospital wastewaters are fed to the equalization/prescreening (EP) process in which gross suspended solids are removed. In addition, the EP process equalizes time-varying hydraulic loading and concentration variations to result in a more uniform feed to the UF process. In the UF process the suspended and dissolved solids with a molecular weight greater than 15,000 are separated to minimize the fouling and maintenance of the RO membranes. The function of the RO process is to remove most of the dissolved organics with a medium molecular weight of 150 to 15,000. The low molecular weight organic solids remaining in the RO permeate are finally oxidized in the O_3/UV process to meet the water quality specifications for nonpotable use: 5 mg/l total organic carbon (TOC) and 10 mg/l chemical oxygen demand (COD), or less. The HC process is used to maintain 5 mg/l free-residual chlorine in the product reuse water.

The typical distribution of TOC, COD and total solids concentrations for the hospital composite wastewater is also shown in Figure 2. The numbers in parentheses are the typical rejection percents for each unit process. The overall contaminant removal rates projected are 98.9% for TOC, 99.5% for COD and 98.5% for total solids.

Figure 3 is a block diagram of the unit processes employed in the Potable/Discharge Mode. The WPS performs two separate, independent functions simultaneously: (1) potable water production from natural fresh or brackish water and (2) hospital wastewater treatment to protect the environment from toxic waste discharge. A total of nine processes are included in both treatment trains. The RO process is the main stage of the potable water treatment while the UF process is the heart of the hospital wastewater treatment for discharge.

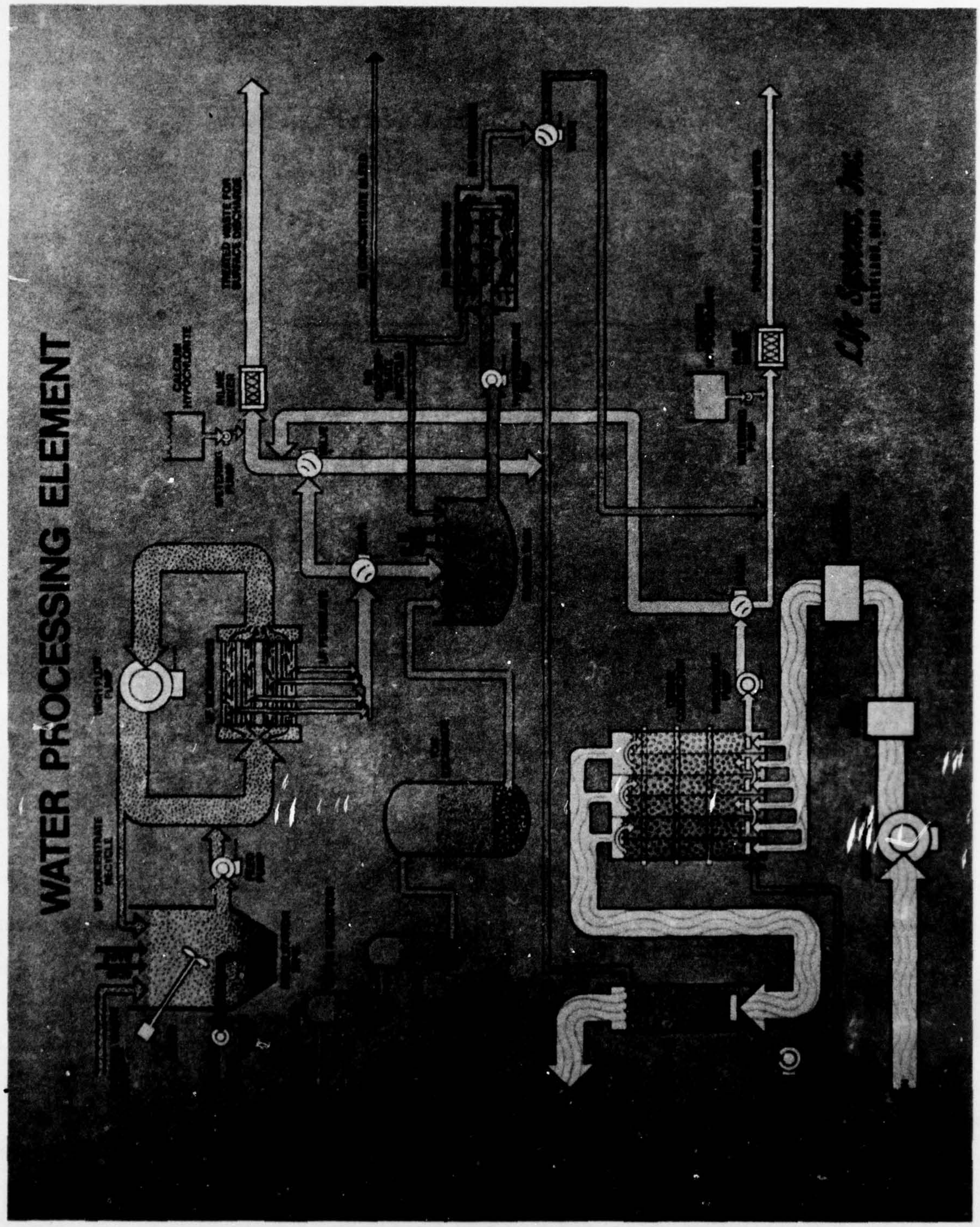


FIGURE 1 WPS PILOT PLANT FLOW DIAGRAM

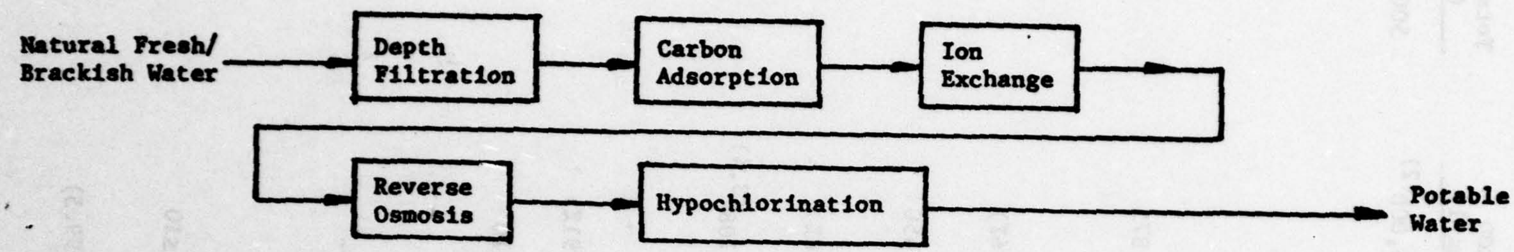
TABLE 1 OPERATIONAL MODES OF THE WATER PROCESSING SYSTEM

Operational Mode	Function	Product Recovery
1. Reuse	• Treatment and Recycle of Nonsanitary Hospital Wastewaters	85%
2. Potable/ Discharge	• Treatment of Natural Fresh and Brackish Waters for Potable and Nonpotable Use	90%
	• Treatment and Discharge to the Environment of Nonsanitary Hospital Wastewaters	95%

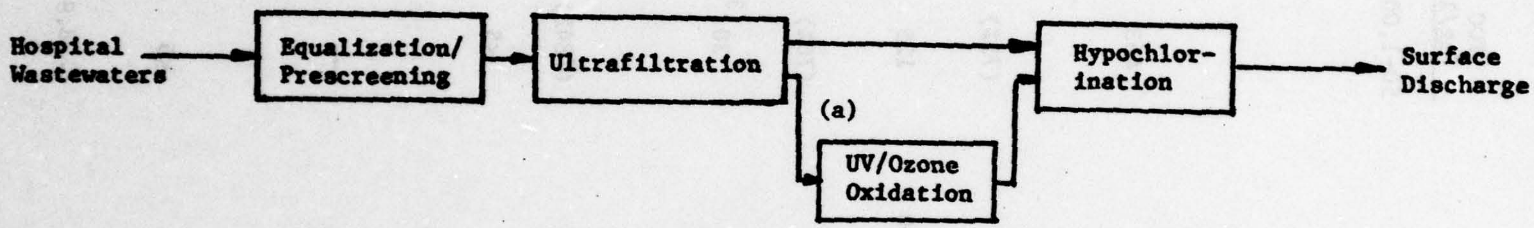
	TOC (mg/1)	COD (mg/1)	Total Solids (mg/1)
Nonsanitary Hospital Wastewaters	50-1,000[2]	300-6,000[2]	500-4,200[2]
↓			
Equalization/ Prescreening (EP)			
↓	463	1,875	1,240[2]
Ultrafiltration (UF)	(73%)	(76%)	(26%)
↓ MW ≤15,000	125	450	918
Reverse Osmosis (RO)	(76%)	(76%)	(98%)
↓ MW ≤150	30[3,4]	108[3,4]	18
UV-Ozone Oxidation (O_3/UV)	(≥84%)	(≥91%)	--
↓	≤5	≤10	--
Hypochlorination (HC)	--	--	--
↓			
Nonpotable Reuse Water	≤5	≤10	--
<u>Total Removal %</u>	(≥98.9)	(≥99.5)	(≥98.5)

FIGURE 2 UNIT PROCESSES INVOLVED IN REUSE MODE

(1) POTABLE WATER



(2) SURFACE DISCHARGE



(a) For wastes with high organic loading such as kitchen, lab, X-ray and composite.

FIGURE 3 WPE POTABLE/DISCHARGE MODE UNIT PROCESSES

Each train has its own HC unit. The O_3/UV process in the surface discharge train is used only for certain wastewaters with a high organic loading.

Natural water pretreatment consists of (1) depth filtration, (2) carbon adsorption and (3) ion exchange. The primary function of the depth filtration process is to remove suspended solids from the natural water stream. The carbon adsorption column is employed to destroy bacteria and organics (humic acid) which may foul the ion exchange resin. The hardness of the influent water is reduced in the ion exchange column. The functions of other processes are basically the same as those described in the Reuse Mode.

The WPS pilot plant is one of the most advanced water treatment systems in which a number of state-of-the-art technologies and the most recent advances in water processing have been integrated into a compact design. It has most of the prototype WPS features which can be transported to a point of mission via conventional routes such as standard cargo trucks, external helicopter loads, railroad, ship or cargo aircraft. In addition to the treatment of field Army hospital wastewaters and natural waters, the pilot plant also can be used as a test bed for the general purpose of water treatment.

The pilot plant employs an advanced instrumentation concept which is highlighted by a minicomputer-based automatic control and monitor system and by the capability of the fault detection/isolation and performance trend analysis. For the safety of the system itself and its operator, the WPS is protected from damages which may result from: (1) illegal operation by unauthorized personnel, (2) any mistakes (unauthorized commands) of unskilled operators and (3) component failures or any abnormal operating conditions. The startup and operation of the system is accomplished by pressing a single button after a valid password is entered through a keyboard panel. The keyboard panel and a cathode-ray tube screen on the instrumentation unit serve as a communication tool between the system and the operator. A number of flexibilities such as semiautomatic instrumentation and manual overrides for major components are also incorporated for pilot plant testing. The pilot plant can be operated at a remote terminal with all of its control, monitor and data acquisition benefits.

UV/OZONE OXIDATION UNIT

The primary objective of the O_3/UV Unit is to destroy and eliminate organic contaminants in the process waters. In the Reuse Mode the O_3/UV Unit is the third treatment unit for the hospital wastewaters pretreated in both the WTU and the WPU. In the Potable/Discharge Mode it serves as a supplementary unit of the WTU to produce a safe discharge water from certain hospital wastewaters with high organic concentrations. The O_3/UV process has been designed to meet the objective in the Reuse Mode of operation since it is the worst case.

The projected variations of the contaminant concentrations in feed water streams (WPU effluent) are 5-110 mg/l for TOC and 16-460 mg/l for COD. The overall contaminant removal efficiencies for the hospital composite wastewater are greater than 84% for TOC and 91% for COD.

Process Description and Design

Figure 4 is a flow schematic of the O_3/UV Unit. Hospital wastewaters treated in either the WPU or the WTU are fed to the precontactor in which they are pretreated with the residual O_3 contained in the off-gas of the main O_3 contactor. The pretreated water is then pumped through a heat exchanger to the six-stage O_3 contactor where the residual organic impurities are oxidized to harmless carbon dioxide (CO_2) and water by O_3 and UV light. The water flows in a co- and counter-current fashion through one stage after another. The product water is finally transferred to an HC unit. The O_3-air mixture from an O_3 generator is fed to the spargers located at the bottom of the O_3 contactor and vented through the precontactor to atmosphere.

The dimensions of the precontactor are 36 x 10 x 78 inches. It has a wet volume of 100 gal to provide a 33-minute space time (mean residence time) for liquid. The liquid level sensors located in the precontactor maintain the water level at 63 to 66 inches. The O_3 contactor is composed of three reactor modules. Each module, consisting of two stages, is 60 x 10 x 78 inches and contains 20 UV lamps. The nominal UV (253.7 nm) output of a single lamp is rated 26.7 W for a 100-hour life. Each contactor stage has its own sparger which is fabricated from a porous sintered stainless steel plate with a 5 micron pore size. The inlet, outlet and intermodule connections of the O_3 contactor are made by using perforated tubes for a uniform water distribution.

The wet volume of the O_3 contactor was sized by using the following equation obtained as a result of a reaction kinetic study (refer to the next section for details):

$$-r_B = -dC_B/dt = kC_B = k' \bar{p}_A^{1.5} \; Vs^{1.5} \; C_B \qquad (1)$$

where r_B = TOC reduction rate,

C_B = TOC concentration,

t = time,

k, k' = rate constants,

$\bar{p}_A$ = log mean of ozone partial pressure in the reactor, and

Vs = air superficial velocity.

Since water flow through the reactor closely approximates the ideal backmix flow under the design conditions, multiple stages are desired to reduce the reactor volume. For backmix flow reactors the concentration-time curve (so-called F curve) is represented by

$$F = C/C_o = 1 - e^{-\theta} \qquad (2)$$

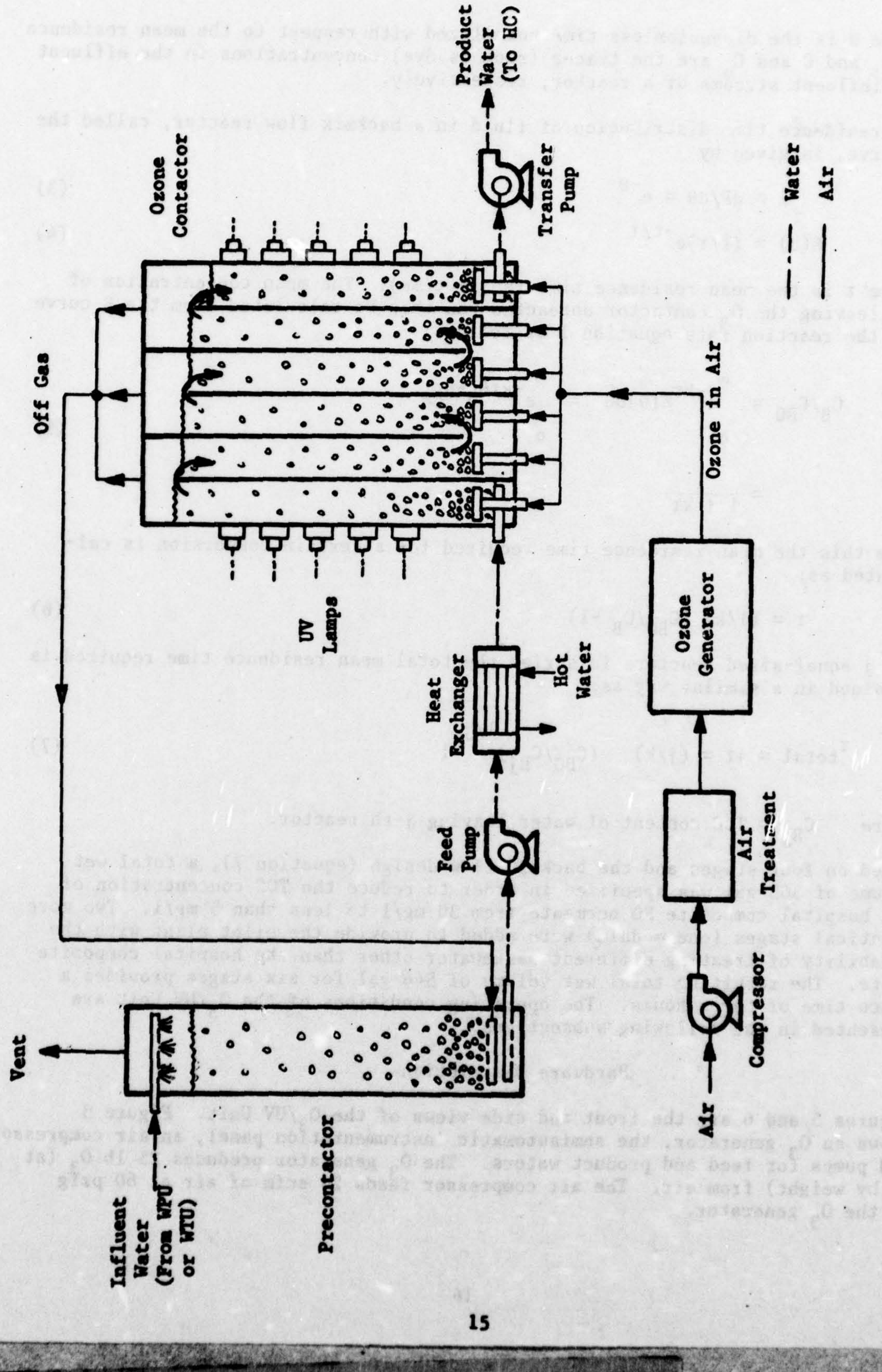


FIGURE 4 UV/OZONE OXIDATION UNIT FLOW SCHEMATIC

where θ is the dimensionless time normalized with respect to the mean residence time, and C and C_o are the tracer (such as dye) concentrations in the effluent and influent streams of a reactor, respectively.

The residence time distribution of fluid in a backmix flow reactor, called the E curve, is given by

$$E = dF/d\theta = e^{-\theta} \tag{3}$$

or

$$E(t) = (1/\tau)e^{-t/\tau} \tag{4}$$

where τ is the mean residence time (space time). The mean concentration of TOC leaving the O_3 contactor unreacted can then be calculated from the E curve and the reaction rate equation 1 as follows:

$$C_B/C_{BO} = \int_o^{\infty} e^{-kt}E(\theta)d\theta = \int_o^{\infty} e^{-k\tau\theta}e^{-\theta}d\theta = \frac{1}{1 + k\tau} \tag{5}$$

From this the mean residence time required for a certain conversion is calculated as:

$$\tau = (1/k)\ (C_{BO}/C_B - 1) \tag{6}$$

For j equal-sized reactors in series the total mean residence time required is obtained in a similar way as:

$$\tau_{total} = j\tau = (j/k)\left[(C_{BO}/C_{Bj})^{1/j} - 1\right] \tag{7}$$

where C_{Bj} = TOC content of water leaving j-th reactor.

Based on four stages and the backmix flow design (equation 7), a total wet volume of 363 gal was specified in order to reduce the TOC concentration of the hospital composite RO permeate from 30 mg/l to less than 5 mg/l. Two more identical stages (one module) were added to provide the pilot plant with the capability of treating different wastewater other than the hospital composite waste. The resulting total wet volume of 544 gal for six stages provides a space time of three hours. The operating conditions of the O_3/UV Unit are presented in the following subsections.

Hardware Description

Figures 5 and 6 are the front and side views of the O_3/UV Unit. Figure 5 shows an O_3 generator, the semiautomatic instrumentation panel, an air compressor and pumps for feed and product waters. The O_3 generator produces 25 lb O_3 (at 1% by weight) from air. The air compressor feeds 24 scfm of air at 60 psig to the O_3 generator.

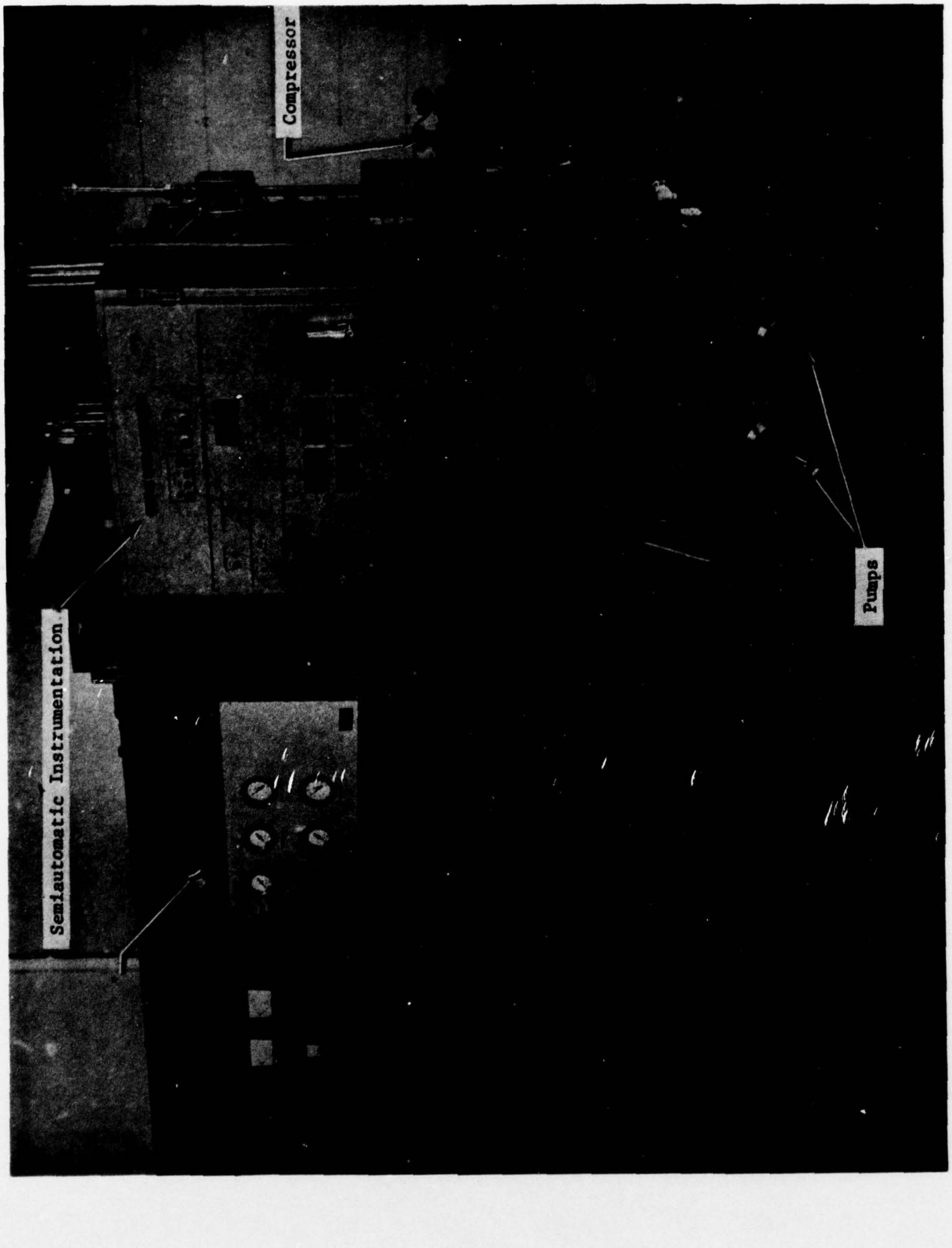


FIGURE 5 UV/OZONE OXIDATION UNIT, FRONT VIEW

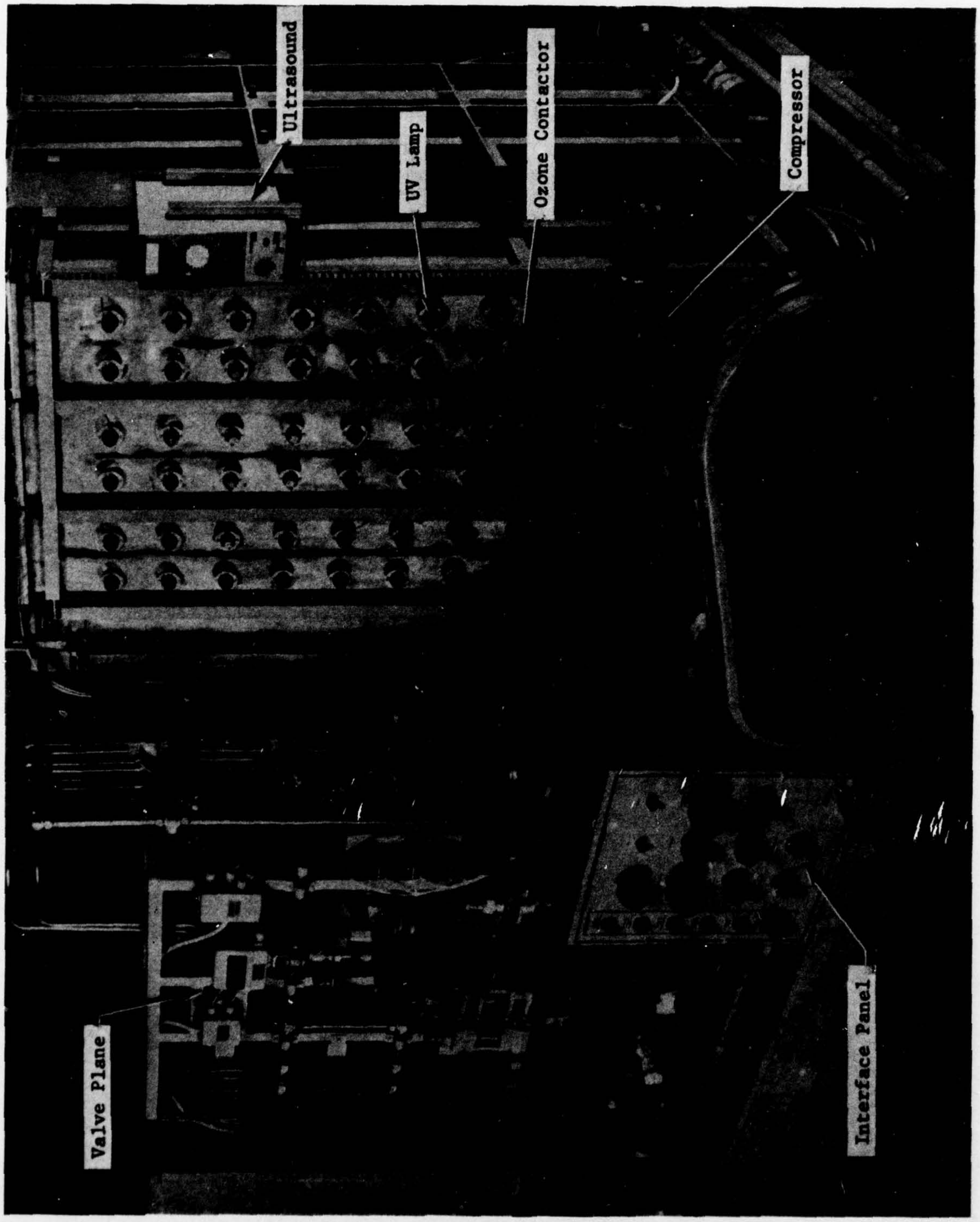


FIGURE 6 UV/OZONE OXIDATION UNIT, SIDE VIEW

Figure 6 shows the O_3 contactor, UV lamps, an ultrasound generator, the air compressor, the valve plane and the interface panel. All inputs and outputs of the O_3/UV Unit go through the interface panel shown in Figure 7. The O_3 contactor, consisting of three reactor modules, is 61 x 40 x 79 inches. Each module has two stages and 20 UV lamps. Electric power for the UV lamps is provided by 30 ballasts. The total wet volume of the O_3 contactor is 544 gal. The ultrasound generator is incorporated into the first stage to enhance the O_3 mass transfer rate. The semiautomatic instrumentation panel shown in Figure 8 is highlighted by seven automatic fail-safe shutdown controls, eight digital readout monitors, ten warning and alarm lights and 26 controls for pumps, valves and UV lamps.

Operation

The O_3/UV Unit can be operated in three modes: (1) Stand Alone, (2) Integrated Semiauto and (3) Integrated Auto. In the Stand Alone mode the O_3/UV Unit operates as a self-contained unit to evaluate the effectiveness of the UV/O_3 oxidation for the general purpose of water treatment. In the Integrated modes it operates as a subsystem of the WPS.

System power is the only connection needed in the Stand Alone mode. With both main and pump power turned on, operation of the unit is initiated by pressing the RESET button on the front panel. All valve switches should be placed in their proper positions before turning on the prime movers. A wastewater feed pump (not included in the O_3/UV Unit, but should be provided along with a wastewater source) should then be turned on to fill the precontactor. When the precontactor is nearly filled with wastewater, as monitored through a sight glass, the water feed pump for the O_3 contactor should be turned on. The O_3 contactor effluent pump is turned on when the last stage of the O_3 contactor is full. As flow develops, those switches should be placed in the AUTO position for the automatic shutdown controls to function. The O_3 generator, the pH pumps and the UV lamps are then turned on by setting corresponding toggle switches to the ON positions. Adjustments for the flow rates of both air and wastewater and for the power setting on the O_3 generator should be made as needed. The ultrasonic generator also can be turned on, if desired. The setpoints for operating conditions can be varied for parametric testing by the use of the digital potentiometers located inside the control panels. Operation of the O_3/UV Unit in the Integrated Semiauto mode is basically the same as that in the Stand Alone mode and will not be detailed here.

In the Integrated Auto mode the O_3/UV Unit is connected through two cables to the Automatic Instrumentation Unit which then places it under direct control of the automatic instrumentation. The switches and shutdown circuits of the O_3/UV Unit are inoperative and the automatic instrumentation controls startup, operation and shutdown of the O_3/UV Unit. The startup and operation of the system is accomplished by pressing a single button after a wastewater source is selected. Detailed descriptions of the Automatic Instrumentation Unit and the WPS as well as their operation can be found elsewhere.[5-7]

The nominal operating conditions of the O_3/UV Unit are summarized in Table 2. No temperature control is planned in the precontactor, though it has been implemented for a flexible operation. For baseline operation the pH of waste-

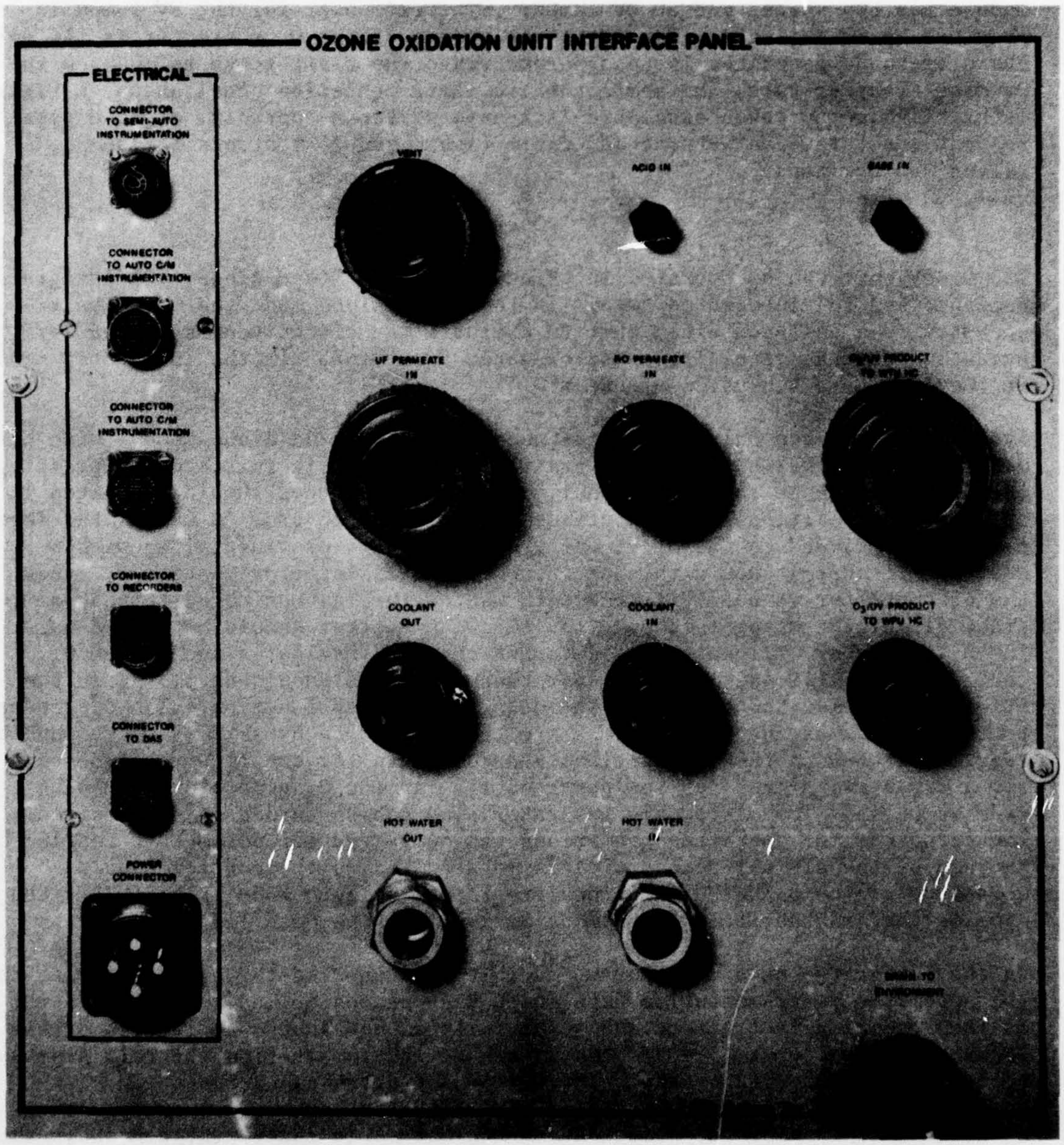


FIGURE 7 UV/OZONE OXIDATION UNIT INTERFACE PANEL

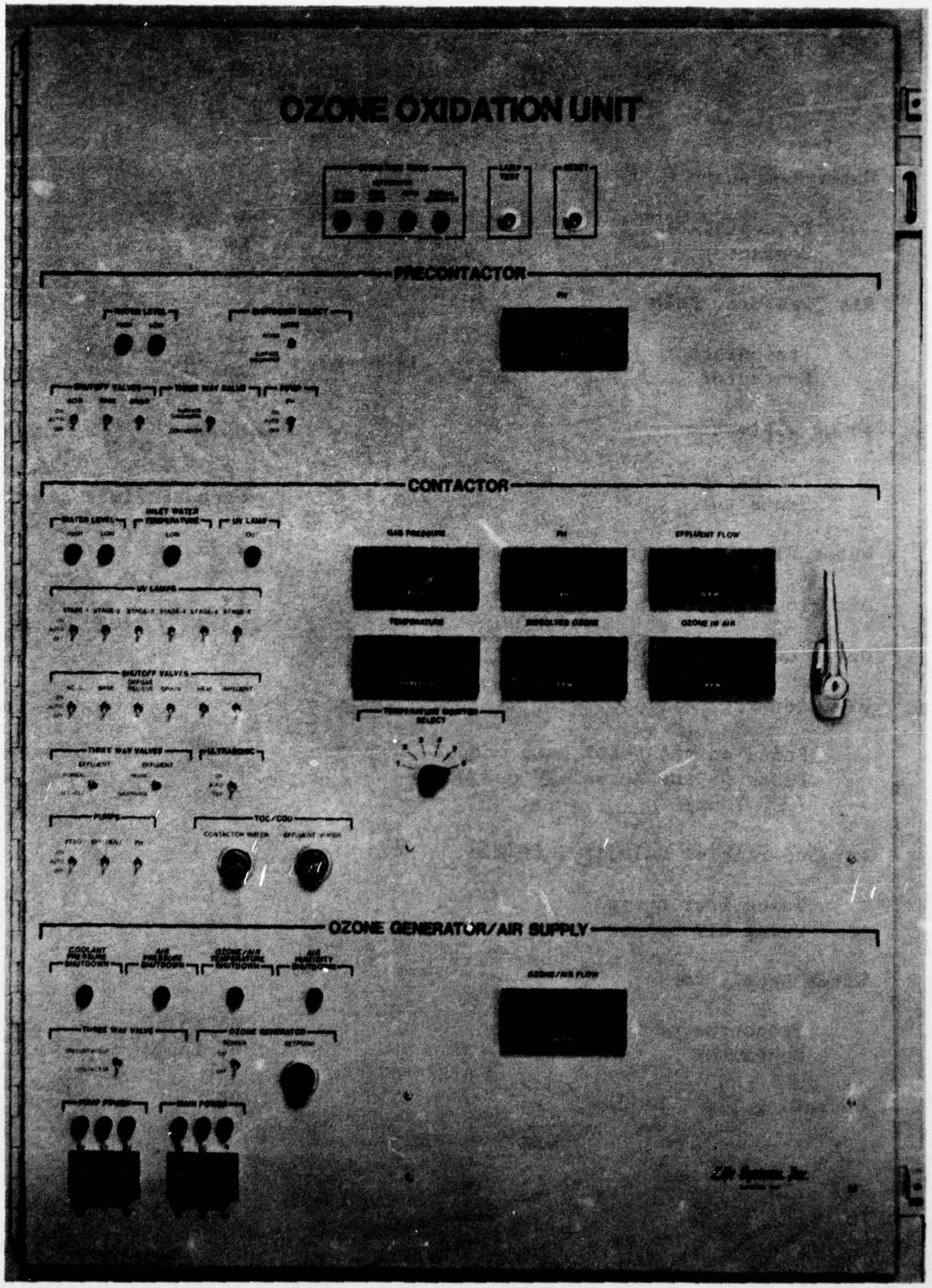


FIGURE 8 UV/OZONE OXIDATION UNIT SEMIAUTOMATIC INSTRUMENTATION

TABLE 2 NOMINAL OPERATING CONDITIONS OF THE UV/OZONE OXIDATION UNIT

Water Temperature, F	
Precontactor	60 to 127
Contactor	86
Air Pressure, psia	
Precontactor	16
Contactor	20
pH of Wastewater	
Precontactor	9
Contactor	Uncontrolled
Water Flow Rate, gpm	2.93
Air Flow Rate, scfm	24
Ozone Concentration, wt. %	1.0
UV Intensity, W/l	
Based on the total lamp output	1.89
Based on the actual UV output (253.7 nm)	0.78
Air Superficial Velocity, ft/min	
Using four stages	2.1
Using six stages	1.4
Water Level, in	
Precontactor	63 to 66
Contactor	68 to 72
Operating Time, hr/day	20

water is controlled only in the precontactor, but provisions were made for a pH control in any stage of the O_3 contactor. The UV intensity based on the actual UV output at the wavelength of 253.7 nm is 0.78 W/l. It is defined as the ratio of the total UV output for all the UV lamps to the total wet volume of the O_3 contactor. The O_3/UV Unit operates 20 hours a day. The water loss by vaporization was estimated to be approximately 0.5%.

The O_3/UV Unit is protected from catastrophic damages due to component failures or any abnormal operating conditions. The unit will be automatically shut down as any alarm conditions defined in Table 3 develop. The cause for a shutdown is monitored with the alarm lamps on the instrumentation panel.

The O_3/UV Unit is a highly versatile, transportable pilot plant with a number of benefits incorporated for scientific data development and performance evaluation. Table 4 lists some of the highlights and benefits of the O_3/UV instrumentation for each mode of operation.

Control/Monitor Instrumentation

Both automatic and semiautomatic instrumentations were incorporated into the O_3/UV Unit to control and monitor the system performance. Only the semiautomatic instrumentation will be described in this section. The objective of the semiautomatic instrumentation was to provide a pilot testing capability for evaluation of the O_3/UV performance.

Control Features

The major control features incorporated in the O_3/UV Unit are:

1. Automatic fail-safe shutdown is initiated by nine alarm conditions (Table 3).
2. Automatic temperature control
3. Automatic pH control
4. Automatic control of water levels
5. Variable UV intensity
8. A total of 26 control switches for pumps, valves and UV lamps are incorporated on the front instrumentation panel

Monitor Features

The following monitor features were incorporated in the O_3/UV Unit:

1. Water pH in both the precontactor and the contactor
2. Water temperature at six locations of the contactor
3. Water flow rate

TABLE 3 SHUTDOWN DEFINITION AND INDICATION

No.	Parameters		Alarm Condition	Alarm Lamp
1	Precontactor Water Level		$\leq$42 in	Water Level Low
2	Contactor (last stage) Water Level		$\leq$42 in	Water Level Low
3	Contactor Air Pressure		$\geq$10 psig	Not Available
4	Coolant Pressure (O_3 generator)	or	$\leq$15 psig $\geq$35 psig	Coolant Press Shutdown
5	Air Pressure (O_3 generator)	or	$\leq$12 psig $\geq$25 psig	Air Pressure Shutdown
6	Air Temperature (O_3 generator)		$\geq$120 F	Ozone/Air Temp. Shutdown
7	Air Humidity (O_3 generator		Dew Point Higher than 0 F	Air Humidity Shutdown

TABLE 4 HIGHLIGHTS/BENEFITS OF THE O_3/UV INSTRUMENTATION

Highlights/Benefits	Operating Mode: Stand Alone	Integrated Semiauto	Integrated Auto
Controls			
• Minicomputer-based Automatic Instrumentation			X
• A Single Button Startup			X
• Automatic Shutdown Controls in Case of Emergency	X	X	X
• Automatic pH Control	X	X	X
• Automatic Temperature Control	X	X	X
• Remote ON/OFF CONTROL		X	X
• Remote CONTROL			X
• Variable UV Intensity	X	X	X
Monitors			
• Written Communication between Operator and the System			X
• Fault Detection/Isolation and Trend Analysis			X
• Remote Monitoring			X
• Digital and Analog Readouts	X	X	

4. Contactor pressure

5. Ozone concentrations in air and water

6. Ozone/air flow rate

7. A total of ten light indicators provide warning and alarm conditions.

UV/OZONE OXIDATION OF ORGANICS IN WATER

The hospital wastewaters contain a variety of toxic chemical compounds. The UF and RO processes are capable of reducing the concentration of many of these compounds to low levels (30 mg/l TOC and 108 mg/l COD for the hospital composite). However, the processed reuse water must be essentially free of organics and inorganics which might be detrimental to man. A concentration level of 5 mg/l TOC and 10 mg/l COD has been suggested as an appropriate water quality specification. The O_3/UV has been demonstrated to be one of the most viable and cost-effective means of polishing the RO permeate to meet the required TOC and COD levels as established for the allowable concentration limits.[3,8]

The expected concentrations of the hospital composite wastewater after UF and RO treatments are shown in Table 5. The X-ray film fixer/developer and methanol are the predominant components as they contribute nearly 77% of the total TOC. Along with acetone and urea, the top five components contribute almost 94% of the total TOC.

The main objective of the O_3/UV process in the Reuse Mode of the WPS operation was to reduce TOC from 30 mg/l to less than 5 mg/l (84% removal) and to reduce COD from 108 mg/l to less than 10 mg/l (91% removal). In addition, the O_3/UV process accomplishes disinfection (100% kill) and complete removal of color and foam.

Reaction Mechanism

The O_3/UV of the hospital wastewater is a heterogeneous system in that O_3 in gas phase is contacted with organics in the liquid phase. Under ordinary test conditions organics may be assumed to be insoluble in the gas phase. Hence, reactions occur in the liquid phase and O_3 has to be dissolved in liquid to react with the organics in the liquid phase.

The reaction mechanisms of organic compounds with O_3/UV in an aqueous solution are very complicated and are not thoroughly understood yet. Hewes and Davidson[9] reported that the rate of organic oxidation increased at the conditions which accelerate the decomposition of O_3. It also has been suggested by Hoigne and Bader[10] and by Peleg[11] that the decomposition products of O_3 in water may be more powerful oxidation agents than O_3 itself. The decomposition of O_3 in water is favored at a higher alkaline pH or at a higher temperature. However, the latter can adversely affect the rate of organic oxidation due to a reduced solubility of O_3 in water. The effect of pH on the O_3 decomposition rate in water is shown in Table 6.

TABLE 5 ORGANIC CHEMICAL COMPOSITION OF SYNTHETIC HOSPITAL COMPOSITE WASTEWATER

	RO Permeate	TOC mg/l	COD mg/l
X-Ray Film Developer	283 μl/l	18.42	64.80
X-Ray Film Fixer	283 μl/l		
Methanol	16 μl/l	4.76	19.05
Acetone	5 μl/l	2.50	8.70
Urea	12.0 mg/l	2.40	9.60
Acetic Acid	2.8 μl/l	1.15	3.15
Phenol	0.4 mg/l	0.31	0.95
Ethanol	0.5 μl/l	0.20	0.82
N,N-Diethyl-m-toluamide	0.2 mg/l	0.15	0.52
Oleic Acid	0.1 μl/l	0.06	0.23
Diethyl Ether	0.1 μl/l	0.05	0.18
Total		30.0	108.0

TABLE 6 EFFECT OF pH ON HALF-LIFE OF OZONE IN WATER

pH	Half-life, min	
	Stumm[12]	Hoigne and Bader*[10]
4.0		350
6.0		50
7.6	41	
8.0		3.33
8.5	11	
8.9	7	
9.2	4	
9.7	2	
10.0		0.33
10.4	0.5	

* pH adjustment by 0.5M sodium phosphate buffer

One of the most effective methods to accelerate the O_3 decomposition is use of UV light. Ozone absorbs UV light and decomposes very rapidly in water. The UV-absorption coefficient of O_3 measured by Schiff[13] is shown in Figure 9. A large absorption coefficient of O_3 at the peak wavelength of UV light (253.7 nm) nm) is noted. The effect of UV light on the O_3 decomposition is well demonstrated in Figure 10 by McCarthy.[8] As UV light is turned on the dissolved O_3 concentration in water drops almost instantaneously to less than 0.2 mg/l. The UV intensity (Iuv) was 2 W/l based on the total lamp output.

Ozone can directly oxidize a large number of organics. It can oxidize alcohols through aldehydes to acids. It can also attack carbon-carbon double bonds of an olefin to form an ozonide which, after hydrolysis and reduction, gives two molecules of aldehydes or ketones. A mechanism for the reaction of O_3 with unsaturated organics has been proposed by Criegee.[14]

If organics in dilute aqueous solution are oxidized only by a direct reaction with O_3 the accelerated decomposition of O_3 should retard the oxidation rate. This hypothesis contradicts the observations of Hewes and Davidson[9] and of other investigators.[15-17] It is postulated that organics can be oxidized both by a direct oxidation with O_3 and by reactions with the decomposition products of O_3, but that the latter reactions are the predominant reaction pathways under UV radiation. In fact, the probability that organic molecules collide and react with O_3 molecules in a very dilute aqueous solution is low compared with that for abundant water molecules. In addition, the decomposition rate with a sufficient supply of UV energy appears to be far greater than the rate of direct organic oxidation.[18] The hypothetical reaction scheme is illustrated in Figure 11.

When irradiated by UV light O_3 in an alkaline aqueous solution appears to decompose to hydroxyl radicals mostly by the following reactions.[19]

$$O_3 + h\nu = O_2^* + O^* \tag{8}$$

$$O^* + H_2O = 2OH^\cdot \tag{9}$$

where * indicates an excited state. Without UV radiation the O_3 decomposition may be initiated with a lower yield by the hydroxide ion as proposed by several investigators.[10,20,21] The hydroxyl radical ($OH^\cdot$) which has a higher oxidation potential than O_3 is very reactive and seems to play a major role in the succeeding oxidations of organics. There are a number of indications that the reactions of O_3 in aqueous solutions are quite similar to those of the hydroxyl radical.[11] Hoigne and Bader[10] have shown that the relative reaction rate of two competing reactions for ozonation in alkaline aqueous solution is roughly the same as that for the hydroxyl radical reaction. Further, they concluded that the hydroxyl radicals become the main oxidative species for the test conditions leading to prior O_3 decomposition.

The hyroxyl radicals thus formed are then consumed on a competitive basis either for the oxidation of organics or for the radical-radical reactions because they are highly reactive. The reaction mechanism for the organic oxidation is not known. It has been suggested that the hydroxyl radicals may undergo hydrogen abstraction reactions with aliphatic compounds.[22] The resulting organic radical may react further to produce an alcohol:

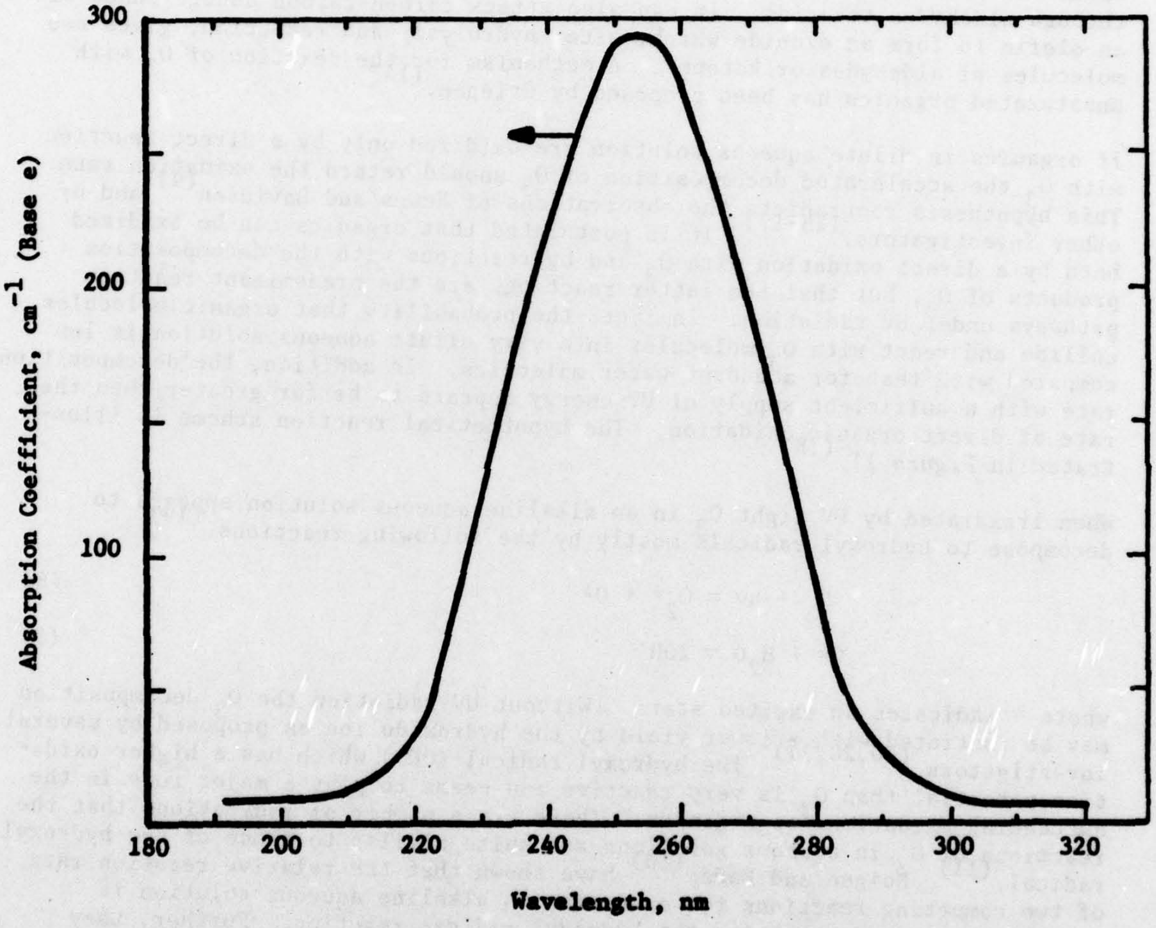


FIGURE 9 COMPARISON OF UV LAMP OUTPUT WITH UV-ABSORPTION BY OZONE[(13)]

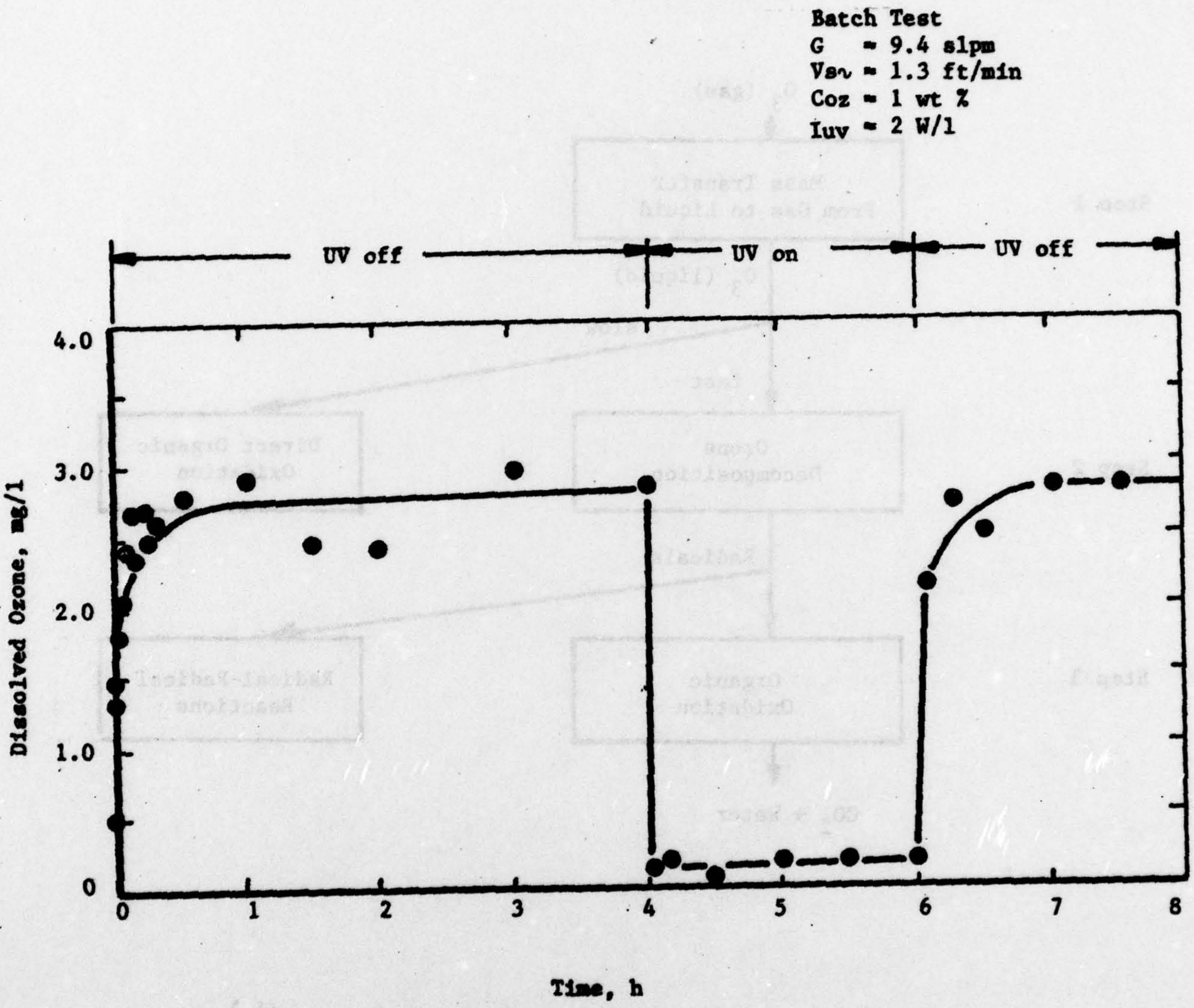


FIGURE 10 DISSOLVED OZONE CONCENTRATION IN TAPWATER[8]

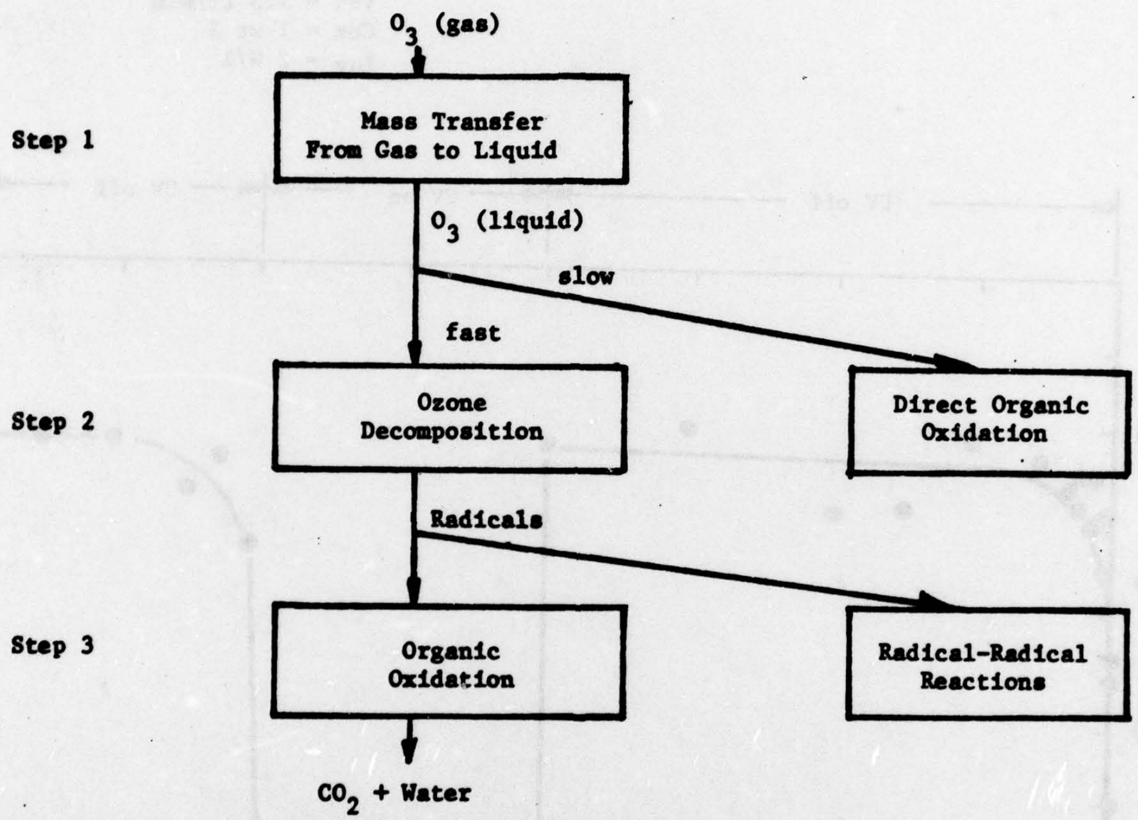


FIGURE 11 PROPOSED REACTION SCHEME FOR UV-OZONE OXIDATION[18]

$$RH + OH^{\cdot} = R^{\cdot} + H_2O \quad (10)$$

$$R^{\cdot} + OH^{\cdot} = ROH \quad (11)$$

In successive abstraction of hydrogens, addition of hydroxyl radicals or oxygen (which is present almost in any ozonation system) and rearrangement of unstable intermediates, alcohols may be oxidized through aldehydes to acids, as the experimental data by Chian and Kuo[23] for the UV-ozonation of methanol indicate. They identified formaldehyde (HCHO) and formic acid (HCOOH) as the intermediate products for the UV-ozonation of methanol. Further oxidation of acids would result in decarboxylation to produce carbon dioxide and water. The oxidation of methanol therefore may proceed as follows:

$$CH_3OH \xrightarrow[hv]{OH^{\cdot}} HCHO \xrightarrow[hv]{OH^{\cdot}} HCOOH \xrightarrow[hv]{OH^{\cdot}} CO_2 + H_2O \quad (12)$$

Chemical Oxygen Demand is naturally reduced as the oxidation proceeds. However, no TOC reduction is realized until decarboxylation occurs.

In addition to the decomposition of O_3 UV light can decompose a number of aldehydes and ketones having a carbonyl group according to the following reactions of Norrish Type I and II:

Type I $\quad R_1COR_2 + hv = R_1 + R_2^{\cdot}CO^{\cdot} \quad (13)$

$$= R_1CO^{\cdot} + R_2^{\cdot}$$

Type II

$$R_1COCH_2CH_2CH_2R_2 + hv = R_1COCH_3 + CH_2{=}CHR_2 \quad (14)$$

The free radicals formed in the Type I reaction are believed to react with solvent or another radical. Thus the O_3/UV of acetone may proceed from the photochemical decomposition:

$$CH_3COCH_3 + hv = CH_3CO^{\cdot} + CH_3^{\cdot} \quad (15)$$

followed by

$$CH_3^{\cdot} + OH^{\cdot} = CH_3OH \quad (16)$$

$$CH_3CO^{\cdot} + OH^{\cdot} = CH_3COOH \quad (17)$$

Methanol may be oxidized as previously outlined. Oxidation of acetic acid may then proceed as follows:

$$CH_3COOH \xrightarrow[hv]{OH^{\cdot}} \begin{matrix} CH_2OH \\ COOH \end{matrix} \xrightarrow[hv]{OH^{\cdot}} \begin{matrix} CHO \\ COOH \end{matrix} \xrightarrow[hn]{OH^{\cdot}} \begin{matrix} COOH \\ COOH \end{matrix} \xrightarrow[hn]{OH^{\cdot}} CO_2 + H_2O \qquad (18)$$

In fact, McCarthy[8] reported that all intermediates except $CH_2OHCOOH$ were identified during UV-ozonation of acetone.

The short-lived, reactive hydroxyl radicals can recombine upon mutual collision. A probable mechanism for the radical-radical reactions (here being called a "suicidal reaction" of free radicals) could be

$$OH^{\cdot} + OH^{\cdot} \underset{hn}{=} H_2O_2 \qquad (19)$$

$$H_2O_2 + OH^{\cdot} = H_2O + HO_2^{\cdot} \qquad (20)$$

$$HO_2^{\cdot} + OH^{\cdot} = H_2O + O_2 \qquad (21)$$

The hydroperoxyl radical ($HO_2^{\cdot}$) is not so reactive and does not appear to make any contribution to organic oxidations. This type of suicidal reaction would then compete with the reactions of organic oxidations.

Mathematical Model of Mass Transfer and Reaction Kinetics

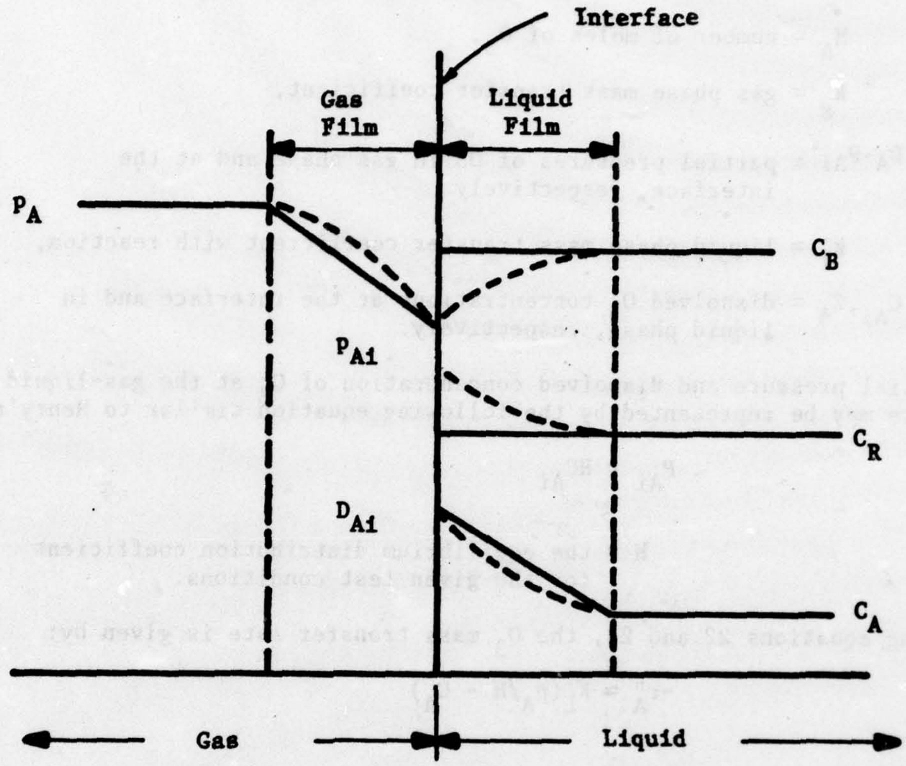
An attempt was made to develop a mathematical model on O_3 mass transfer and reaction kinetics. To avoid lengthy measurements of concentration variation for each component, TOC was selected as a representative indication for the total concentration of various organic compounds in the hospital composite wastewater. In addition, further simplifications were made by assuming:

1. TOC is insoluble in gas.
2. The film theory is applicable to describe the mass transfer rate of O_3.
3. The TOC reduction in the liquid film is small enough that the overall reaction rates may be estimated from the bulk concentrations.
4. The decomposition rate of O_3 is far greater than its reaction rate with organics.

The profiles of reactant concentrations used for modeling are illustrated in Figure 12. The dotted lines indicate the expected actual concentrations of reactants.

Mass Transfer and Decomposition of Ozone

According to the film theory the mass transfer rate of O_3 from the gas to liquid phase can be written as:



A = Ozone; B = TOC; R = Radical

FIGURE 12 CONCENTRATION PROFILES ASSUMED FOR MODELING

$$-r_A'' = -\frac{1}{S}\frac{dM_A}{dt} = k_g(p_A - p_{Ai}) = k_l'(C_{Ai} - C_A) \qquad (22)$$

where S = total surface area of gas bubbles,

M_A = number of moles of O_3,

k_g = gas phase mass transfer coefficient,

p_A, p_{Ai} = partial pressures of O3 in gas phase and at the interface, respectively

k_l' = liquid phase mass transfer coefficient with reaction,

and C_{Ai}, C_A = dissolved O_3 concentrations at the interface and in liquid phase, respectively.

The partial pressure and dissolved concentration of O_3 at the gas-liquid interface may be represented by the following equation similar to Henry's law:

$$P_{Ai} = HC_{Ai} \qquad (23)$$

where H = the equilibrium distribution coefficient for the given test conditions.

Combining equations 22 and 23, the O_3 mass transfer rate is given by:

$$-r_A'' = K_L'(p_A/H - C_A) \qquad (24)$$

where

$$1/K_L' = 1/Hk_g + 1/k_l' \qquad (25)$$

Based on the liquid volume it can be rewritten:

$$-r_{A,m} = -ar_A'' = K_L'a\ (p_A/H - C_A) \qquad (26)$$

where $a = S/V$ and V = the liquid volume.

The decomposition rate of O_3 can be represented as equation 27, assuming j-th order with respect to the concentration of dissolved O_3 in liquid.

$$-r_{A,d} = k_d C_A^{\,j} \qquad (27)$$

where

k_d = a rate constant. Then, a mass balance for O_3 gives:

$$r_A = dC_A/dt = r_{A,d} - r_{A,m} \tag{28}$$

$$= K_L^{'}a\ (p_A/H - C_A) - k_d C_A^{\,j}$$

where

r_A = the rate of change of dissolved O_3 concentration.

If c moles of free radicals are formed per decomposition of one mole of O_3 i.e.,

$$A + hn = cR \tag{29}$$

$$(A = O_3;\ R = \text{free radical})$$

the rate of formation for free radicals, which lead to Step III reactions (Figure 11), can be written as:

$$r_{R,f} = c(-r_{A,d}) = c\ k_d C_A^{\,j} \tag{30}$$

The value of c will be 2 if every O_3 molecule decomposed reacts with water according to equations 8 and 9. In reality, however, c is believed to be less than two since some oxygen atoms may not be excited enough to react with water.

Organic Oxidation and Radical Reactions

The free radicals formed are then consumed on a competitive basis either for the oxidation of organics or for the suicidal reactions among radicals. For the oxidation of organics (Step III-1) the stoichiometry and the rate equation for the disappearance of TOC were approximated as:

$$B + bR \overset{k_o(B)}{=} \text{Products } (CO_2 + H_2O) \tag{31}$$

$$-r_B = -dC_B/dt = k_o C_R^{\,m} C_B^{\,n} \tag{32}$$

where k_o = the rate constant based on B=TOC. The rate of disappearance for free radicals is then:

$$r_{R,o} = br_B = -bk_o C_R^{\,m} C_B^{\,n} \tag{33}$$

It was assumed that the reaction is m-th order with respect to radical concentration (C_R) and n-th order for TOC (C_B).

The rate of the suicidal reactions for free radicals (Step III-2) was formulated as equation 34, assuming l-th order reaction with respect to the concentration of radicals:

$$-r_{R,s} = k_s C_R^{\,l} \qquad (34)$$

Consequently, the rate of change for the radical concentration can be written as:

$$r_R = dC_R/dt = r_{R,f} + r_{R,o} + r_{R,s} \qquad (35)$$

$$= ck_d C_A^{\,j} - bk_o C_R^m C_B^n - k_s C_R^{\,l}$$

Simplified Model

The O_3/UV process for experiments performed is a semibatch operation where O_3-entrained air with a constant concentration of ozone is continuously passed through a reactor containing wastewater. In semibatch operations the concentration of the reactant present in continuous flow does not change appreciably with time. With the passage of time TOC concentration will fall but the O_3 concentration will remain relatively unchanged as long as the decomposition reaction is not the only rate-limiting step. Consequently, the analysis is restricted to the case in which the overall rate is not controlled solely by the decomposition reaction. Under such quasi-steady-state conditions:

$$r_A = dC_A/dt \cong 0 \qquad (36)$$

and from equation 28

$$(k_d/K_L'a)\, C_A^{\,j} + C_A = p_A/H \qquad (37)$$

If j is given the algebraic equation 37 can be solved for C_A. Differential equations 32 and 35 can then be solved for C_R and C_B if the constants l, m and n are determined from experiments.

For a simple case the decomposition reaction of O_3 with the UV light in an alkaline aqueous solution was assumed to be first order as reaction 8 and measurements by several investigators suggest.[12,24,25] From equation 37 the dissolved O_3 concentration is then given by:

$$C_A = p_A/(H(1 + k_d/K_L'a)) \qquad (38)$$

and the differential equations to be solved are:

$$-r_B = -dC_B/dt = k_o C_R^m C_B^n \quad (32)$$

$$r_R = dC_R/dt = -cr_{A,d} + r_{R,s} + br_B \quad (35)$$

$$-r_{A,d} = k_d C_A \quad (39)$$

$$-r_{R,s} = k_s C_R^1 \quad (34)$$

The analytical solutions for this system still do not appear to be possible. In order to obtain simple analytical solutions two special cases were considered as follows:

Case 1: $C_B = B$

Case 2: $C_B = 0$

Case 1. If TOC concentration is very large compared with other concentrations

$$br_B \text{ JJ } r_{R,s} \quad (40)$$

then equation 35 can be simplified as:

$$r_R = -cr_{A,d} + br_B \quad (41)$$

Since the O_3 decomposition and the organic oxidation are reactions in series, the rate of radical disappearance by oxidation cannot be greater than the rate of formation by O_3 decomposition. Hence, a material balance for radicals should give at a quasi-steady-state condition:

$$cr_{A,d} = br_B \quad (42)$$

or

$$-dC_B/dt = a\, K_L' a p_A/(H(1 + K_L' a/k_d)) \quad (43)$$

where $a = c/b$

Equation 43 can be easily solved to give:

$$C_{BO} - C_B = aK_L' a p_A t/(H(1 + K_L' a/k_d)) \quad (44)$$

where C_{BO} is the TOC concentration at $t = 0$. The rate constant of the O_3 decomposition, k_d, is a function of UV intensity, pH and temperature. At a controlled condition to give $K_L a/k_d$ FF1 such as high UV intensity and high pH, equation 44 can be further simplified to:

$$C_{BO} - C_B = (a\, K_L' a/H) p_A t \quad (45)$$

The analysis implies that the TOC reduction rate is directly proportional to the O_3 partial pressure.

Case 2. As the TOC concentration approaches zero the rate of radical disappearance by oxidation becomes negligible compared with that by suicidal reactions and the decomposition rate should balance with the rate of suicidal reactions. Therefore, the following equations are obtained at a steady-state:

$$r_{R,s} \ Z \ cr_{A,d} \tag{46}$$

$$-dC_B/dt = k_2 p_A^{m/1} C_B^{\ n} \tag{47}$$

where $$k_2 = k_o \left(\frac{cK_L' a/k_s}{H(1 + K_L' a/k_d)} \right)^{m/1}$$

Integration of equation 47 with the following initial condition

$$C_B = C_{BN} \text{ at } t = t_N, \tag{48}$$

results in:

$$\ln(C_{BN}/C_B) = k_2 p_A^{m/1} t \qquad \text{for } n = 1 \tag{49}$$

$$C_B^{\ 1-n} - C_{BN}^{\ 1-n} = (n-1) k_2 p_A^{m/1} t \tag{50}$$

For $K_L' a/k_d FF1$, k_2 is further simplified as:

$$k_2 \ Z \ k_o \ (cK_L' a/Hk_s)^{m/1} \tag{51}$$

The analysis suggests that the rate of TOC reduction is dependent on C_B and p_A.

Application to UV/Ozone Oxidation of Hospital Wastewaters

With a proper selection of operating conditions such as initial TOC concentration, feed gas O_3 concentration and gas flow rate, the reaction of organic oxidation can proceed through three phases with different reaction rates as shown in Figure 13.

Initial Period (Phase I). Unless the mass transfer and decomposition rates of O_3 are so great to result in a high concentration of radicals, the suicidal reactions can be neglected due to the high TOC concentration during the initial period. Hence the model equation for Case 1 may be used to describe the

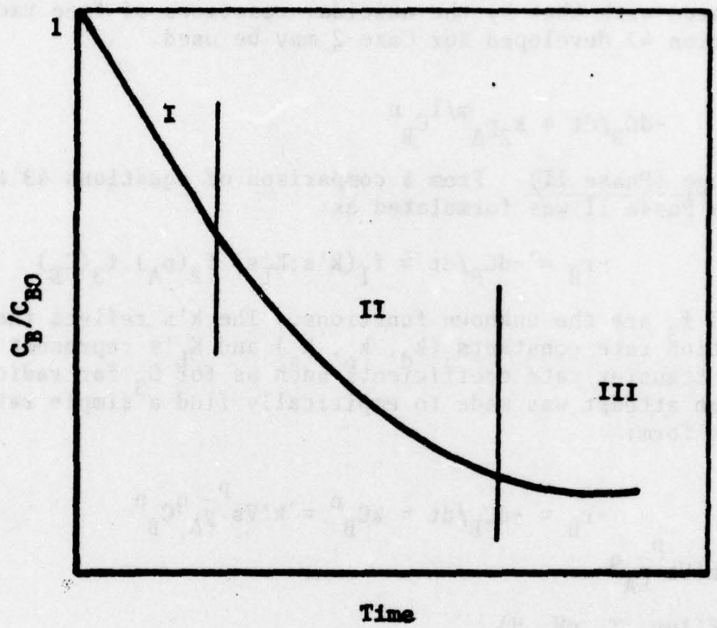


FIGURE 13 UV-OZONE OXIDATION OF HOSPITAL COMPOSITE WASTEWATER

reaction rate in Phase I. Since the UV intensity used in this study was high enough to give $K_L'a/k_d FF1$, equation 45 was used.

$$C_{BO}-C_B = (a\ K_L'a/H)p_A t \tag{45}$$

Tail End (Phase III). At the tail end of the reaction curve the TOC concentration approaches zero and the radical consumption by organic oxidation becomes negligible compared with that by the suicidal reactions of free radicals. Therefore, equation 47 developed for Case 2 may be used.

$$-dC_B/dt = k_2 p_A^{m/1} C_B^{\ n} \tag{47}$$

Intermediate Range (Phase II). From a comparison of equations 43 and 47 the rate equation in Phase II was formulated as:

$$-r_B = -dC_B/dt = f_1(k's;K_L's).f_2(p_A).f_3(C_B) \tag{52}$$

where f_1, f_2 and f_3 are the unknown functions. The k's reflect the influence of various reaction rate constants (k_d, k_o, k_s) and K_L's represent the effects of various mass transfer rate coefficients such as for O_3 for radicals and for TOC. Further, an attempt was made to empirically find a simple rate equation of the following form:

$$-r_B = -dC_B/dt = kC_B^{\ n} = k'Vs^{p}\bar{p}_A^{\ q}C_B^{\ n} \tag{53}$$

where $k = k'Vs^{p}\bar{p}_A^{\ q}$

$k' = f(Iuv, T, pH, H)$,

Vs = gas superficial velocity and

$\bar{p}_A$ = log mean of O_3 partial pressure in the reactor

The UV intensity, Iuv, is defined as:

$$Iuv = \frac{\text{Total output of UV lamp (W)}}{\text{Reactor wet volume (l)}}$$

The superficial velocity term was included in the rate equation to reflect the overall effect of gas flow rate on the mass transfer rate coefficients of various reactants (organics, radicals and O_3) in the liquid film. Experiments conducted to determine the constants (k, p, q and n) are described in the following sections.

Experiments

A series of batch tests were conducted to develop a rate equation for the reduction of TOC in hospital composite wastewater. The experimental setup used for this study is shown in Figure 14. The O_3-air mixture from the O_3

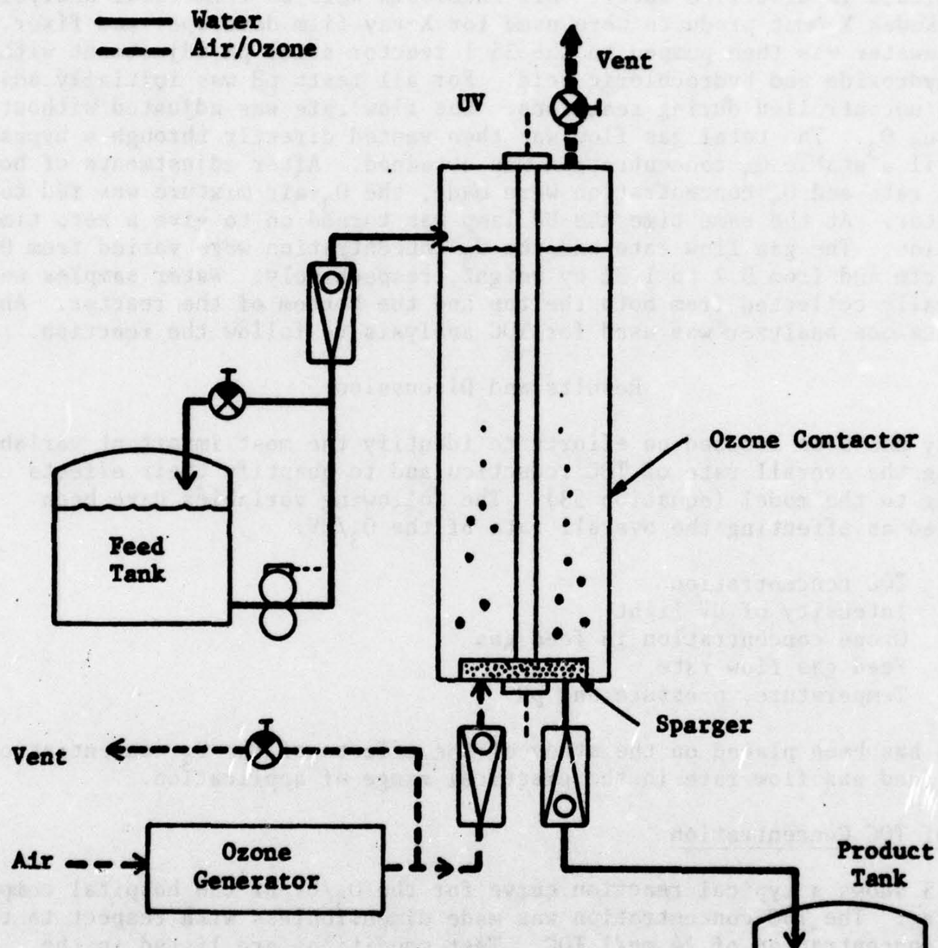


FIGURE 14 SCHEMATIC DIAGRAM OF OZONE CONTACTING SYSTEM

generator was sparged through a six-foot high water column and vented to atmosphere. The O_3 contactor consists of a 6.5 ft long, 6.25 in ID acrylic resin tube, a UV lamp and a sparger fabricated of porous sintered stainless steel. The UV lamp was vertically installed along the center line of the reactor.

The synthetic hospital wastewater was prepared according to Table 5 by dissolving chemicals in distilled water. All chemicals were of commercial analytical grade. Kodak X-Omat products were used for X-ray film developer and fixer. The wastewater was then pumped to the 35 l reactor after pH adjustment with sodium hydroxide and hydrochloric acid. For all tests pH was initially adjusted to 9 and uncontrolled during reactions. Gas flow rate was adjusted without generating O_3. The total gas flow was then vented directly through a bypass line until a stable O_3 concentration was obtained. After adjustments of both gas flow rate and O_3 concentration were made, the O_3-air mixture was fed to the reactor. At the same time the UV lamp was turned on to give a zero time of reaction. The gas flow rate and the O_3 concentration were varied from 0.12 to 0.5 scfm and from 0.7 to 1.3% by weight, respectively. Water samples were periodically collected from both the top and the bottom of the reactor. An organic carbon analyzer was used for TOC analysis to follow the reaction.

Results and Discussion

The study has been focused on efforts to identify the most important variables affecting the overall rate of TOC reduction and to quantify their effects according to the model (equation 53). The following variables have been identified as affecting the overall rate of the O_3/UV:

- TOC concentration
- Intensity of UV light
- Ozone concentration in feed gas
- Feed gas flow rate
- Temperature, pressure and pH

Emphasis has been placed on the study of the effects of the O_3 concentration and the feed gas flow rate in the practical range of application.

Effect of TOC Concentration

Figure 15 shows a typical reaction curve for the O_3/UV of the hospital composite wastewater. The TOC concentration was made dimensionless with respect to the initial concentration of 24 mg/l TOC. Test conditions are listed in the figure. The reaction proceeds through three phases with different rates as postulated in the Mathematical Modeling Section. In Phase II the experimental data follows a straight line reasonably well in a semilog plot of the concentration-time curve. This indicates a first-order reaction with respect to TOC concentration. Therefore, the value of n in equation 53 was estimated as:

$$n = 1 \qquad \text{in Phase II}$$

The slope of the straight line is the overall rate constant k in Phase II. The figure also demonstrates well that O_3/UV effectively reduces the TOC of hospital composite wastewater from 24 mg/l to below 1.5 mg/l within two hours.

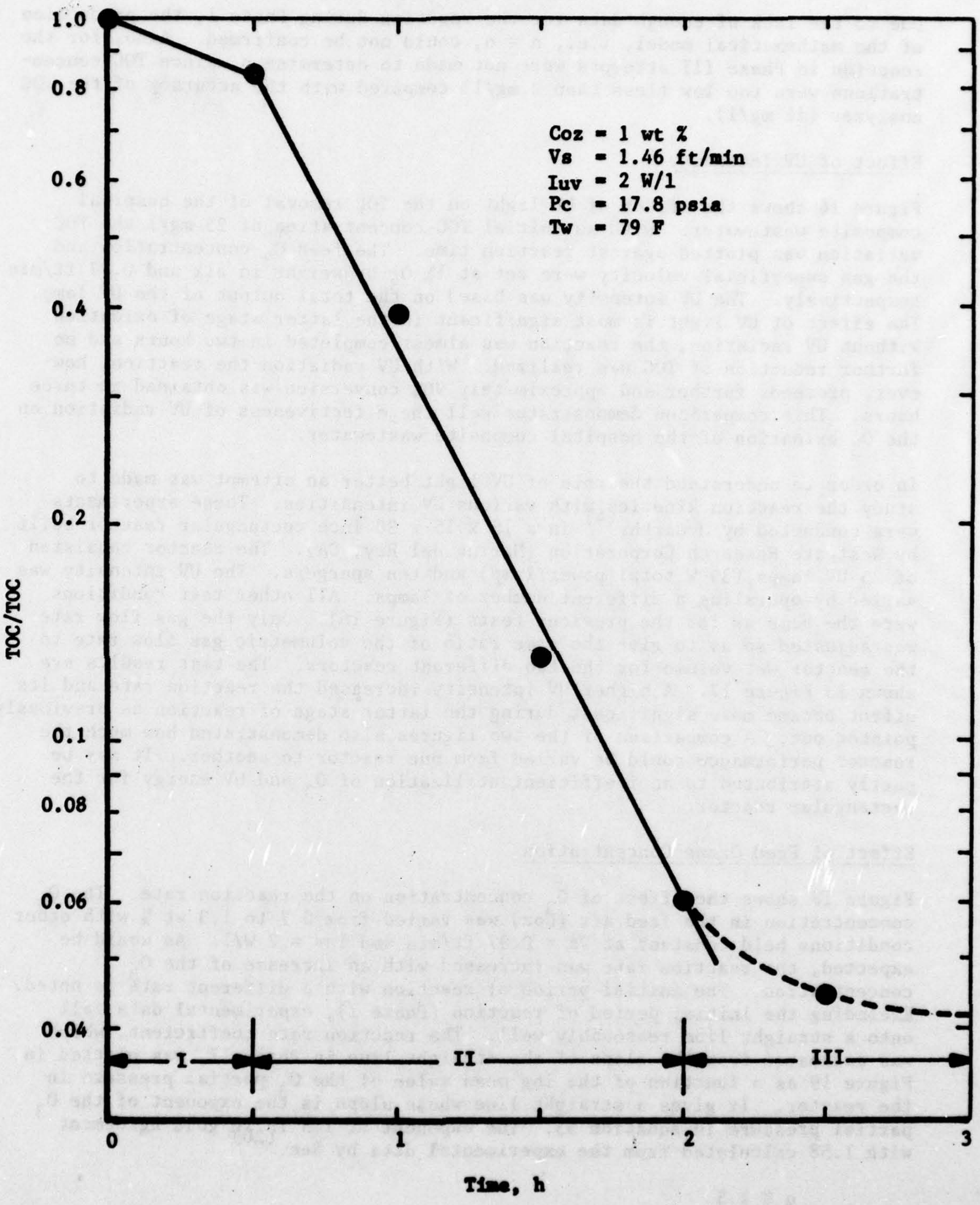


FIGURE 15 UV-OZONE OXIDATION OF HOSPITAL COMPOSITE WASTEWATER

Due to the lack of enough data for the reaction during Phase I, the prediction of the mathematical model, i.e., n = o, could not be confirmed. Also, for the reaction in Phase III attempts were not made to determine n, since TOC concentrations were too low (less than 2 mg/l) compared with the accuracy of the TOC analyzer (±1 mg/l).

Effect of UV Intensity

Figure 16 shows the effect of UV light on the TOC removal of the hospital composite wastewater. With an initial TOC concentration of 25 mg/l the TOC variation was plotted against reaction time. The feed O_3 concentration and the gas superficial velocity were set at 1% O_3 by weight in air and 0.97 ft/min respectively. The UV intensity was based on the total output of the UV lamp. The effect of UV light is most significant in the latter stage of oxidation. Without UV radiation, the reaction was almost completed in two hours and no further reduction of TOC was realized. With UV radiation the reaction, however, proceeds further and approximately 90% conversion was obtained in three hours. This comparison demonstrates well the effectiveness of UV radiation on the O_3 oxidation of the hospital composite wastewater.

In order to understand the role of UV light better an attempt was made to study the reaction kinetics with various UV intensities. These experiments were conducted by McCarthy[4] in a 15 x 15 x 30 inch rectangular reactor built by Westgate Research Corporation (Marina del Rey, CA). The reactor consisted of 25 UV lamps (39 W total power/lamp) and ten spargers. The UV intensity was varied by operating a different number of lamps. All other test conditions were the same as for the previous tests (Figure 16). Only the gas flow rate was adjusted so as to give the same ratio of the volumetric gas flow rate to the reactor wet volume for the two different reactors. The test results are shown in Figure 17. A higher UV intensity increased the reaction rate and its effect became more significant during the latter stage of reaction as previously pointed out. A comparison of the two figures also demonstrated how much the reactor performance could be varied from one reactor to another. It may be partly attributed to an inefficient utilization of O_3 and UV energy for the rectangular reactor.

Effect of Feed Ozone Concentration

Figure 18 shows the effect of O_3 concentration on the reaction rate. The O_3 concentration in the feed air (C_{oz}) was varied from 0.7 to 1.3 wt % with other conditions held constant at Vs = 0.97 ft/min and Iuv = 2 W/l. As would be expected, the reaction rate was increased with an increase of the O_3 concentration. The initial period of reaction with a different rate is noted. Excluding the initial period of reaction (Phase I), experimental data fall onto a straight line reasonably well. The reaction rate coefficient, which was estimated from the slope of the straight line in Phase II, was plotted in Figure 19 as a function of the log mean value of the O_3 partial pressure in the reactor. It gives a straight line whose slope is the exponent of the O_3 partial pressure in equation 53. The exponent of 1.5 is in good agreement with 1.58 calculated from the experimental data by See.[26]

$$q \cong 1.5$$

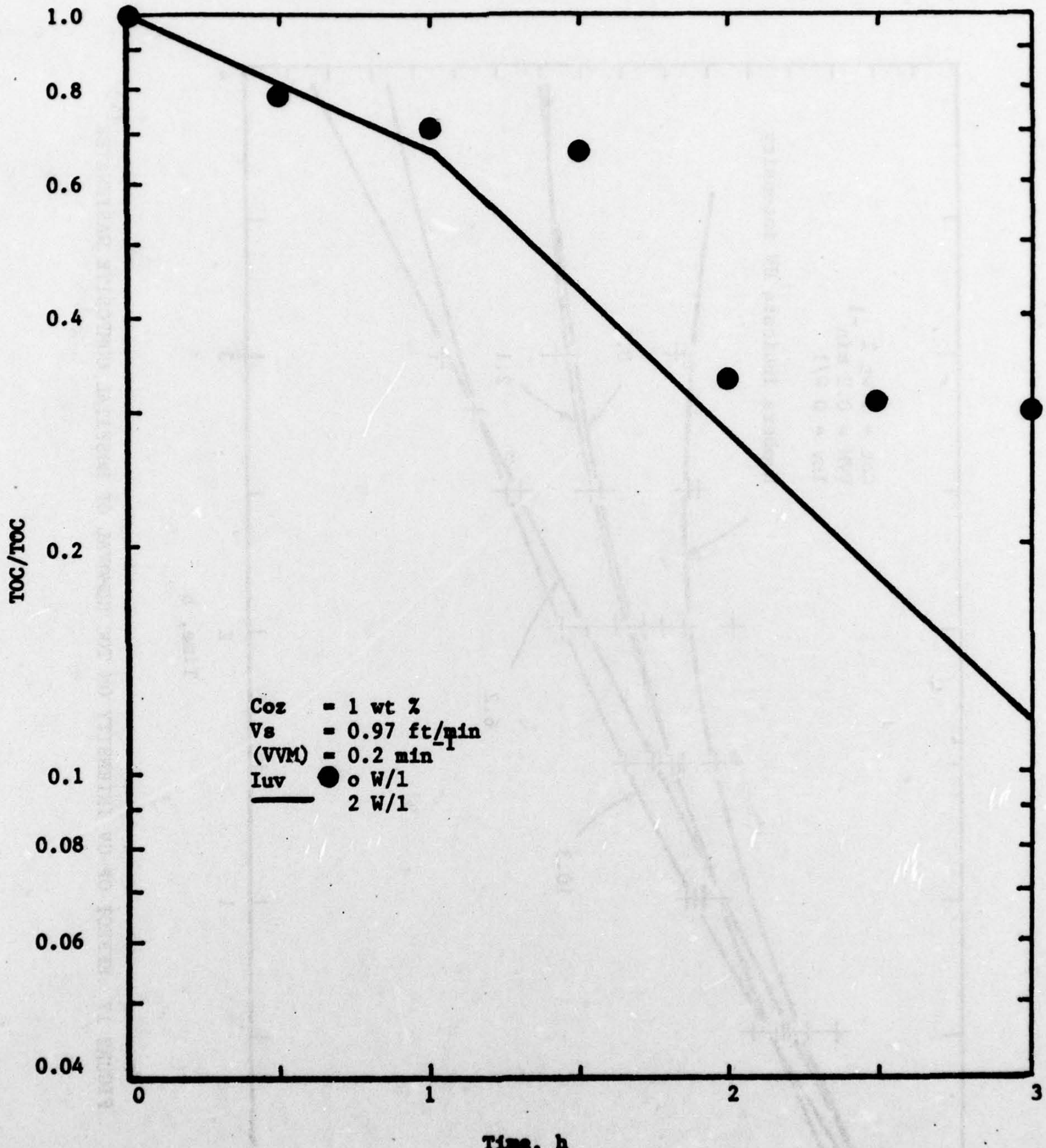


FIGURE 16 EFFECT OF UV INTENSITY ON TOC REMOVAL OF HOSPITAL COMPOSITE

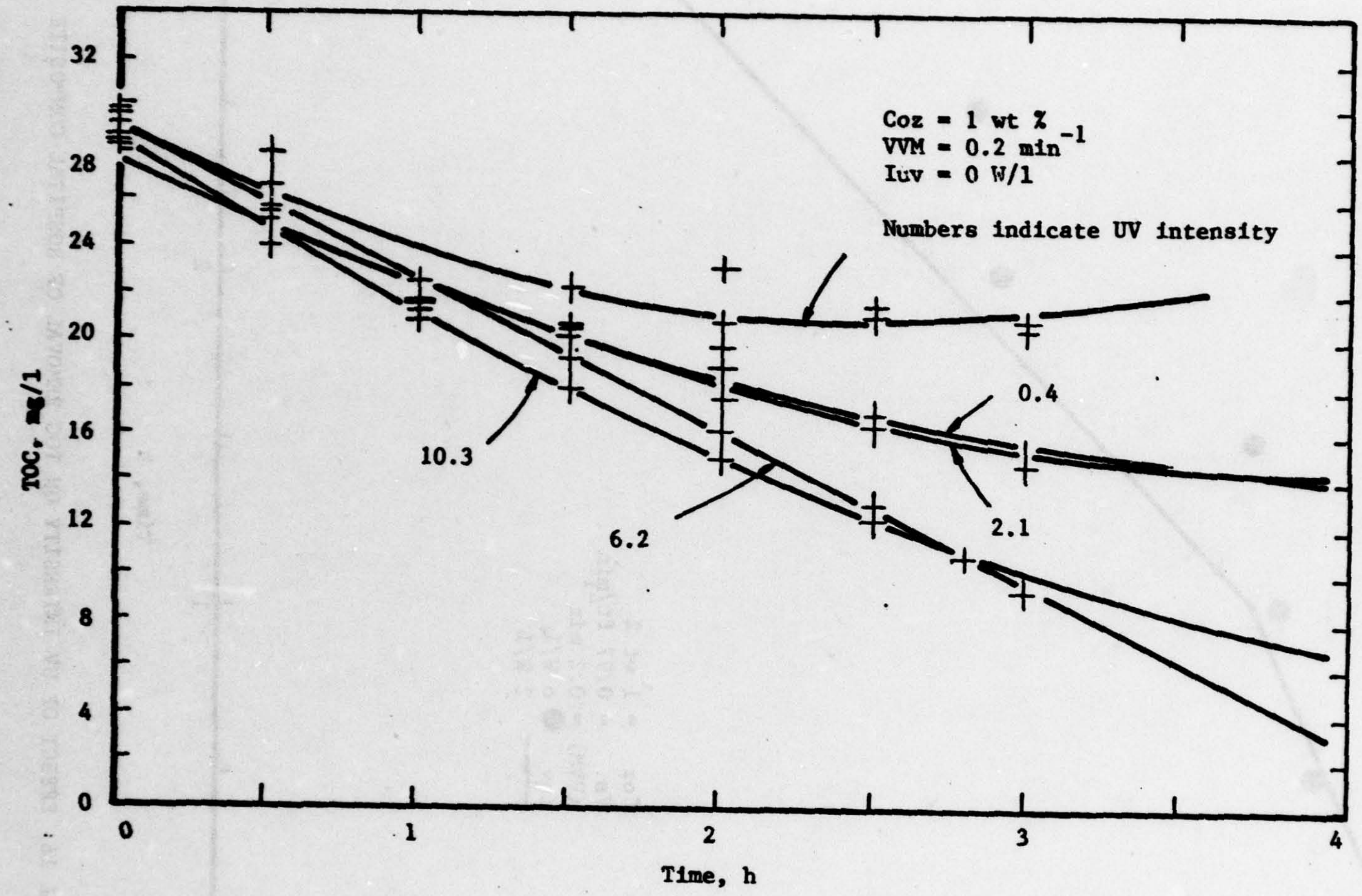


FIGURE 17 EFFECT OF UV INTENSITY ON TOC REMOVAL OF HOSPITAL COMPOSITE WASTEWATER(4)

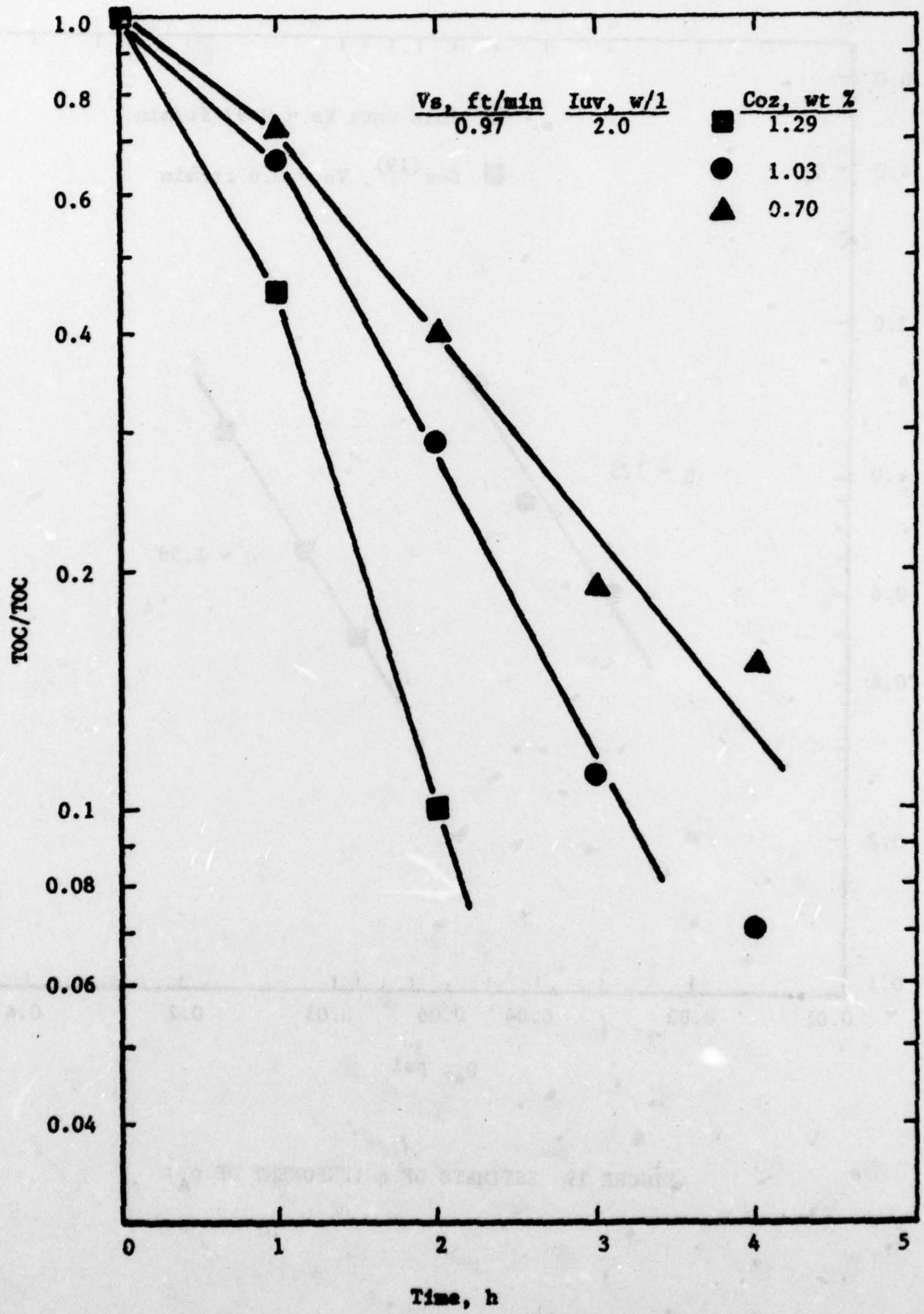


FIGURE 18 EFFECT OF OZONE CONCENTRATION ON TOC REMOVAL OF HOSPITAL COMPOSITE WASTEWATER

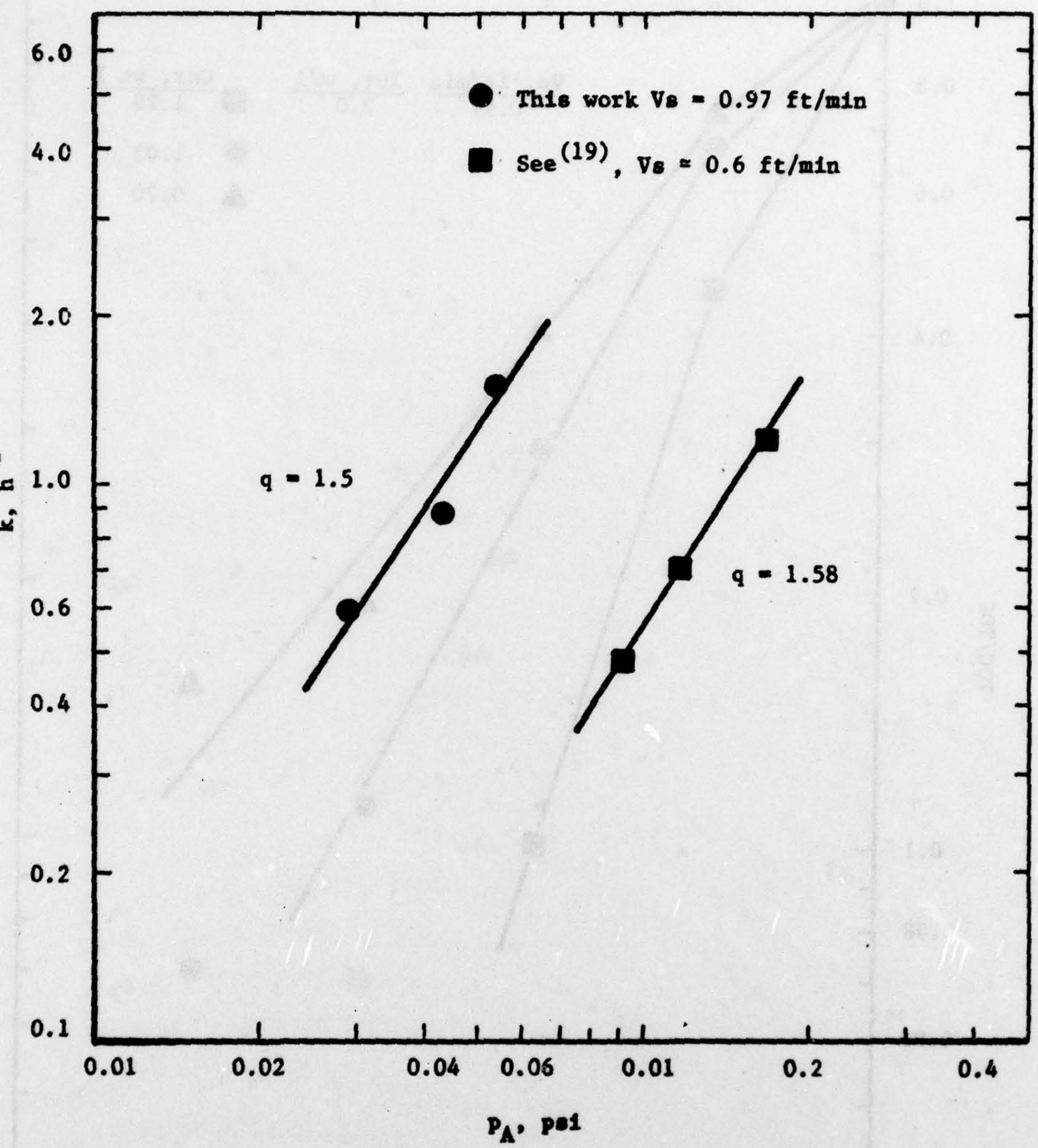


FIGURE 19 ESTIMATE OF q (EXPONENT OF p_A)

Effect of Gas Flow Rate

The effect of gas flow rate on the TOC reduction rate is shown in Figure 20. Only the gas flow rate was varied with other test conditions held constant. The O_3 ozone concentration and the UV intensity were set at 1 wt % and 2 W/l, respectively. As the air flow rate increases, the reaction rate drastically increases. The initial period of reaction with a different rate is again noted. The reaction rates in Phase I are about the same for all flow rates, but the length of the period appears to be reduced as the gas flow rate increases.

The overall reaction rate constant in Phase II was plotted in Figure 21 as a function of the gas superficial velocity. Since the data form a reasonably straight line, the exponent of the gas superficial velocity in the rate equation 53 may be estimated as the slope of the line, i.e.

$$p \cong 1.5$$

Effect of Temperature, Pressure and pH

Higher temperature accelerates the decomposition rate of O_3 in water and usually favors the O_3 oxidation of organics in the hospital composite wastewater. However, it also reduces the solubility of O_3 in water resulting in a lower mass transfer rate of O_3 from gas to liquid phase. Therefore, an optimum temperature may exist for the best overall performance of the process as the measurements by Gollan[2] indicated for the O_3 oxidation of the hospital composite wastewater without using UV light. For the O_3 oxidation with UV radiation, however, the favorable effect of high temperature becomes insignificant due to the strong effect of UV light on the O_3 decomposition and the reaction rate. Therefore, higher temperatures may result in slowing down the reaction rate due to the reduced solubility of O_3. This was confirmed by See.[26] The O_3/UV rate of the hospital composite wastewater at 86 F was reported faster than the rate at 140 F.[26] This finding contrasts with the report by Gollan[2] that the reaction without UV radiation was faster at 140 F than at 86 F. It is, however, cautioned that the above conclusion seems to hold in a temperature range of approximately 68 F to 212 F. If temperature is too low (<68 F) and the UV intensity is not high enough to give negligible concentration of dissolved O_3, the temperature is believed to play a role in the reaction.

Operating pressure has a significant effect on the overall rate of O_3/UV. As the pressure increases the O_3 partial pressure increases and so does the mass transfer rate of O_3 from gas to liquid. In the previous sections it was shown that the overall rate is directly proportional to the O_3 partial pressure in Phase I and to the 1.5th power of that in Phase II. Consequently, a higher operating pressure should increase the overall rate of reaction if all other conditions are held constant. For commercial O_3 generators with a carrier gas supply system, the gas handling capacity is usually limited. Thus, if the pressure is increased the superficial gas velocity is reduced to result in slowing down the overall rate of reaction in Phase II as shown in the previous section. Accordingly, the net effect of increasing pressure becomes insignificant for the reaction in Phase II, though there seems to be a significant gain in Phase I. Experiments are underway to confirm this. Indirect support for

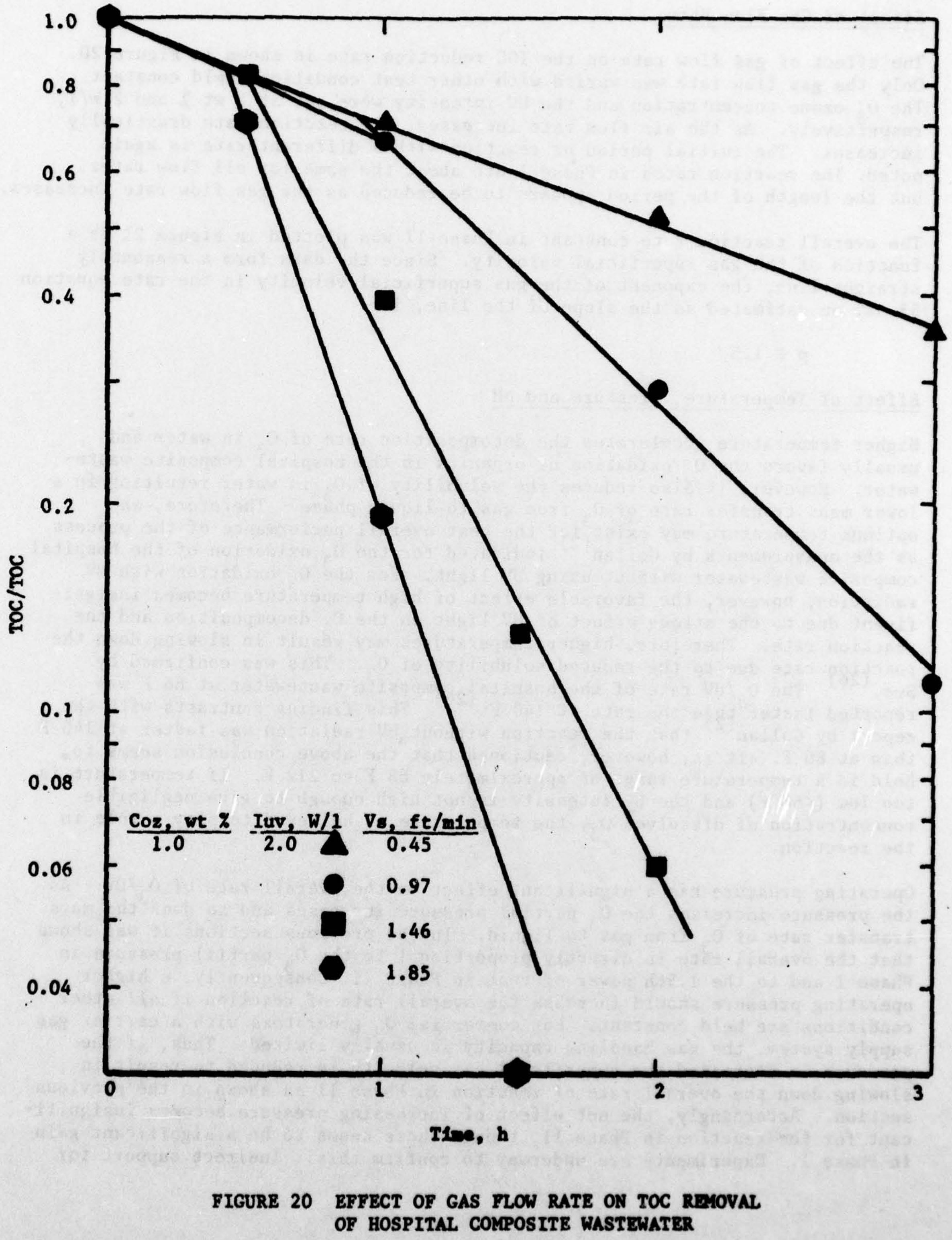


FIGURE 20 EFFECT OF GAS FLOW RATE ON TOC REMOVAL OF HOSPITAL COMPOSITE WASTEWATER

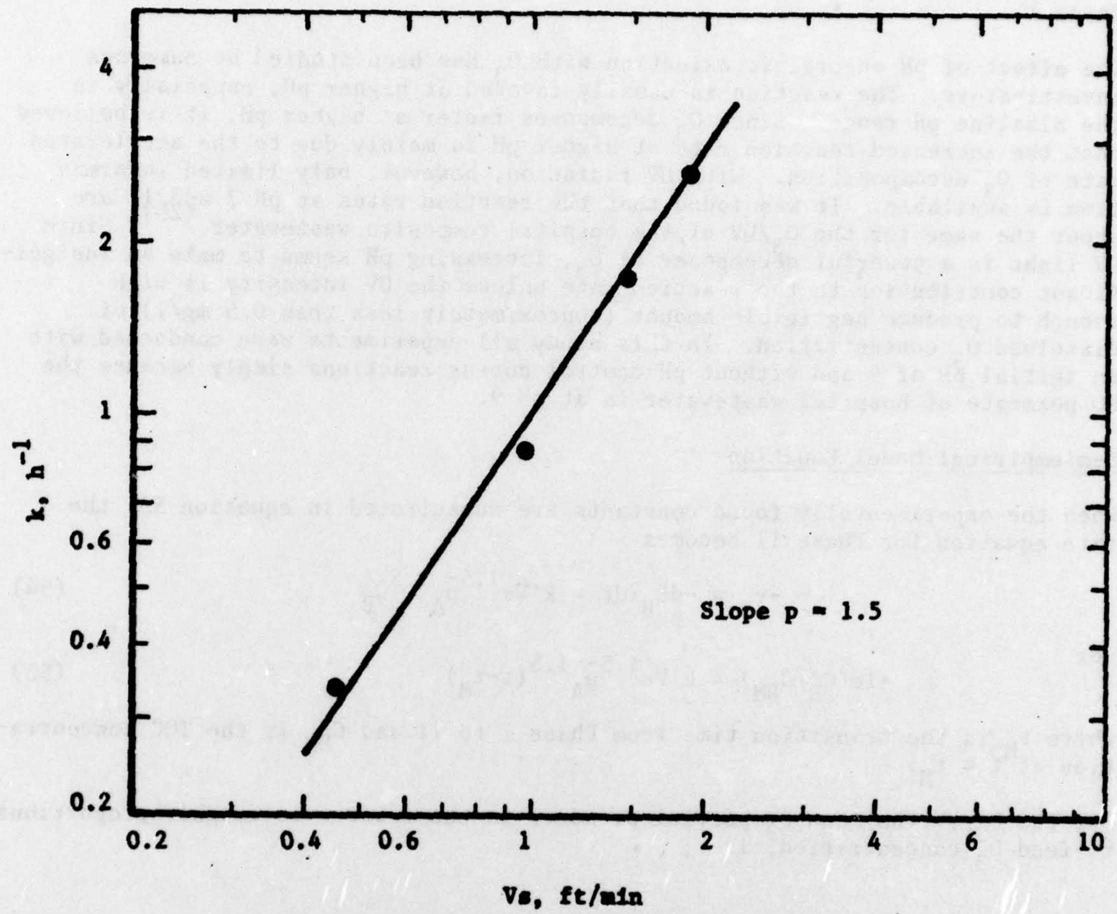


FIGURE 21 ESTIMATE OF p (EXPONENT OF Vs)

this argument can be found from Figures 18 and 20 in that higher O_3 partial pressure due to higher O_3 concentration gives the higher reaction rate, but that the air flow rate has no significant effect on the reaction rate in Phase I.

The effect of pH on organic oxidation with O_3 has been studied by numerous investigators. The reaction is usually favored at higher pH, especially in the alkaline pH range. Since O_3 decomposes faster at higher pH, it is believed that the increased reaction rate at higher pH is mainly due to the accelerated rate of O_3 decomposition. With UV radiation, however, only limited information is available. It was found that the reaction rates at pH 7 and 11 are about the same for the O_3/UV of the hospital composite wastewater.[26] Since UV light is a powerful decomposer of O_3, increasing pH seems to make an insignificant contribution to the reaction rate unless the UV intensity is high enough to produce negligible amount (approximately less than 0.5 mg/l) of dissolved O_3 concentration. In this study all experiments were conducted with an initial pH of 9 and without pH control during reactions simply because the RO permeate of hospital wastewater is at pH 9.

Semiempirical Model Equation

When the experimentally found constants are substituted in equation 53, the rate equation for Phase II becomes

$$-r_B = -dC_B/dt = k'Vs^{1.5}\bar{p}_A{}^{1.5}C_B \qquad (54)$$

or

$$-\ln(C_B/C_{BM}) = k'Vs^{1.5}\bar{p}_A{}^{1.5}(t-t_M) \qquad (55)$$

where t_M is the transition time from Phase I to II and C_{BM} is the TOC concentration at $t = t_M$.

For the O_3/UV the mean O_3 partial pressure in the reactor is roughly proportional to feed O_3 concentration, i.e.,

$$\bar{p}_A \propto Coz$$

and the superifical gas velocity is directly proportional to the mass flow rate of feed gas, M. Thus equation 55 can be written as

$$\begin{aligned} -\ln\,(C_B/C_{BM}) &= k''\,(M\;Coz)^{1.5}(t-t_M) \qquad (56)\\ &= k''\,D^{1.5}(t-t_M) \end{aligned}$$

where the O_3 dosage D is defined by

$$D = M\;Coz \qquad (57)$$

The analysis shows that the TOC reduction rate in Phase II is directly proportional to the TOC concentration and to the 1.5th power of the O_3 dosage.

The model equation 45 for Phase I was not directly tested in this study. However, the dependence of the overall rate on the O_3 concentration, shown in Figure 18, is qualitatively in agreement with the model, since the O_3 concentration is proportional to the O_3 partial pressure.

It was shown in Figure 20 that the overall rate during Phase I was almost independent of the gas flow rate. This suggests that the reaction may take place at the gas-liquid interface or in the immediate vicinity of the interface. When the reaction occurs at the interface and the TOC concentration is very high, the liquid film does not play any role on the overall rate. Accordingly, the effect of the gas flow rate on the mass transfer rate of O_3 becomes insignificant, since the gas flow rate mostly affects the resistance in the liquid film. However, if no surfactants are present in liquid, the gas flow rate can affect the gas film resistance due to a torroidal motion in the gas bubble.

CONCLUSIONS

The following conclusions were drawn from the results of this study:

1. The O_3/UV serving as a final purification step of the WPS makes it possible for the WPS to produce nonpotable reuse water from the nonsanitary wastewaters generated in the field Army medical facilities.

2. The overall reaction for TOC reduction with O_3 and UV light proceeds through three phases with different rates. The reaction in Phase II is important since most TOC reduction occurs in this phase.

3. The reaction in Phase II is first-order with respect to the TOC concentration and 1.5th-order with respect to the O_3 partial pressure.

4. The Phase II reaction also has 1.5th-order dependence on the gas superficial velocity. This suggests that the O_3 mass transfer in the liquid film plays a significant role on the reaction rate. In the tested range the TOC reduction rate is roughly proportional to 1.5th power of the O_3 dosage.

5. The UV light radiation is one of the most effective methods to accelerate the O_3 decomposition in water. The resulting higher decomposition rate of O_3 enhances the organic oxidation rate. This supports the notion that the decomposition products (i.e., hydroxyl radicals) of O_3 may be more powerful oxidation agents than O_3 itself. The effect of UV light is most significant during the latter stage of oxidation.

6. A number of flexibilities implemented in hardware and instrumentation enable the O_3/UV Unit to serve as a test bed for the general purpose of water treatment.

RECOMMENDATIONS

The following recommendations are direct results of this study:

1. Integrated testing of the WPS with simulated hospital wastewaters should be performed to evaluate and characterize the performances of the WPS and the O_3/UV Unit.
2. The performances of the WPS and the O_3/UV Unit should be evaluated with various kinds of wastewaters generated in the other fixed and mobile installations of the U. S. Army.
3. Pilot plant studies should be performed to collect all the data necessary for a prototype system design such as:
    - Effect of the number of contactor stages on performance
    - Effect of variable air flow rates through contactor stages
    - Effect of UV light in the first two stages
    - Effect of ultrasound and pH control
    - Fluid mixing and contacting pattern
    - Ozone mass transfer and reaction kinetics
    - Effect of UV intensity
4. In parallel with the pilot plant studies, the following bench-scale testing is recommended:
    - Study the effect of using a packed tower instead of a sparged column for the precontactor and the first stage of the O_3 contactor
    - Study the effect of the sparger pore size on the bubble sizes, the mass transfer rate, the reaction rate and the power consumption for air compression
5. A preliminary system study for the prototype WPS design should be initiated to guide the pilot plant activities in the right direction.

REFERENCES

1. Lambert, W. P. and McCarthy, J. J., "Ozone Oxidation for Reuse of Army Field Hospital Wastewaters," IOI Forum on Ozone Disinfection, Ozone Press Int., 108, 1977.

2. Gollan, A. Z., McNulty, K. J., Goldsmith, R. L., Kleper, M. H. and Grant, D. C., "Evaluation of Membrane Separation Processes, Carbon Adsorption, and Ozonation for Treatment of MUST Hospital Wastes," Final Report, Contract DAMD17-74-C-4066, ADAO 30057, Walden Research Division of Abcor, Inc., Wilmington, MA, August, 1976.

3. Lee, M. K., "A UV-Ozone Oxidation Kinetic Study and Reactor Design for the Water Processing Element," presented at the French Lick Ozone Conference, sponsored by U. S. Army Medical Research and Development Command, French Lick, IN, LSI ER-349, Life Systems, Inc., Cleveland, OH, August 10, 1977.

4. McCarthy, J. J., "Ozonation of Synthetic Hospital Composite RO and UF Permeate Using the Westgate Unit Reactor Module," Memorandum to W. P. Lambert, May 17, 1977.

5. Lee, M. K., Yang, P. Y., Wynveen, R. A. and See, G. G., "Pilot Plant Development of an Automated, Transportable Water Processing System for Field Army Medical Facilities," Final Report, Contract DAMD17-76-C-6063, ER-314-7-1, Life Systems, Inc., Cleveland, OH, June, 1978.

6. Yang, P. Y., Yeh, J. Y., Powell, J. D. and Wynveen, R. A., "Advanced Instrumentation Development for a Water Processing Pilot Plant for Field Army Medical Facilities," Technical Report, Contract DAMD17-76-C-6063, ER-314-7-4, Life Systems, Inc., Cleveland, OH, June, 1978.

7. See, G. G. and Yang, P. Y., "Water Processing Element Operation Manual," Contract DAMD17-76-C-6063, ER-314-38, Life Systems, Inc., Cleveland, OH, September, 1977.

8. McCarthy, J. J., Cowen, W. J. and Chian, E. S. K., "Evaluation of an Air Stripping-Ozone Contactor System," presented at the 32nd Industrial Waste Conf., Purdue Univ., 1977.

9. Hewes, C. G. and Davison, R. R., "Kinetics of Ozone Decomposition and Reaction with Organics in Water," J. AICHE, 17, 141, 1971.

10. Hoigne, J. and Bader, H., "The Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions," Water Research, 10, 377, 1976.

11. Peleg, M., "The Chemistry of Ozone in the Treatment of Water," Water Research, 10, 361, 1976.

12. Stumm, W., "Ozone as a Disinfectant for Water and Sewage," J. Boston Soc. Civil Engr., 45, 68, 1958.

13. Schiff, H. I., "Laboratory Measurement of Reactions Related to Ozone Photochemistry," Ann. Geophys., t28, Fas. 1, 67, 1972.

14. Criegee, R., "The Course of Ozonazation of Unsaturated Compounds," Record Chem. Progr., 18, 111, 1957.

15. Huibers, D. T. A., McNabney, R. and Halfon, A., "Ozone Treatment of Secondary Effluents from Wastewater Treatment Plants," Fed. Water Pollut. Control Assoc., Report TWR C-4, 1969.

16. Kirk, B. S., McNabney, R. and Wynn, C. S., "Pilot Plant Studies of Tertiary Wastewater Treatment with Ozone," Ozone in Water and Wastewater Treatment, Edited by Evans, R. L., Ann Arbor, MI, 1972.

17. Singer, P. C. and Zilli, W. B., "Ozonation of Ammonia in Wastewater," Water Res., 9, 127, 1975.

18. Lee, M. K., See, G. G. and Wynveen, R. A., "Reaction Kinetics of UV/Ozone with Organic Compounds in Hospital Wastewater," Presented at the Symposium on Advanced Ozone Technology, Sponsored by International Ozone Institute, Inc., Toronto, Canada, LSI ER-345, Life Systems, Inc., Cleveland, OH, November 16-18, 1977.

19. Bamford, C. H. and Wayne, R. P., "Photochemistry in the Liquid Phase," Photochemistry and Reaction Kinetics, edited by Ashmore, P. G., Cambridge, 1967.

20. Weiss, J., "Investigations on the Radical HO_2 in Solution," Trans. Far. Soc., 31, 688, 1935.

21. Gorbenko-Germanov, D. S. and Kozlova, I. V., "Mechanism of Ozone Decomposition in Alkaline Aqueous Media," Dokl. Akad. Nauk. SSR, 210, 851, 1973.

22. Anbar, M., Meyerstein, D. and Neta, P., "Reactivity of Aliphatic Compounds Towards Hydroxyl Radicals," J. Chem. Soc. (B), 742, 1966.

23. Chian, E. S. K. and Kuo, P. P. K., "Fundamental Study on the Post Treatment of RO Permeates from Army Wastewaters," Second Annual Summary Report Contract No. DAMD17-75-C-5006, 1976.

24. Czapski, G., Samuni, A. and Yellin, R., "The Disappearance of Ozone in Alkaline Solutions," Isr. J. Chem., 6, 969, 1968.

25. Rogozhkin, G. I., "Kinetics of Ozone Absorption by Alkaline Solutions," Chem. Abstr., 73, 81108y, 1970.

26. See, G. G., Kacholia, K. K. and Steenson, T. S., "Research and Development of an Ozone Contactor for the Oxidation of Refractory Organics," IOI Forum on Ozone Disinfection, Ozone Press Int., 153, 1977.

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